GEOCHIMICA ET COSMOCHIMICA ACTA

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Orthoclase is likewise sericitized and its alteration is more widespread than with the plagioclase but less intense. Biotite is almost entirely fresh with pleochroism $Z = Y =$ deep brown red and $X =$ pale brown, but inclusions of radioactive zircon are common and give dark green pleochroic haloes; a few biotite crystals have been hydrothermally altered to give green chlorite associated with iron ore.

The accessory minerals include, in order of decreasing abundance, apatite, andalusite, zircon, topaz, fluorite and sphene (rare as in all the Devon and Cornwall granites of Carboniferous age).

Table 1

	1(*R*)	(1*M*)	(1*B*)	1(*S*)	1(*C*)	
SiO_2	72·15	49·25	35·06	48·85	33·59	SiO_2
Al_2O_3	14·84	31·78	18·40	26·29	26·56	Al_2O_3
TiO_2	0·18	0·56	2·16	0·86	0·94	TiO_2
Fe_2O_3	0·41	1·45	4·11	5·95	10·60	Fe_2O_3
MgO	(0·47)	1·31	5·72	1·12	2·63	MgO
FeO	1·47	0·90	18·83	0·60	—	FeO
MnO	(0·05)	0·05	0·65	0·18	0·04	MnO
Na_2O	3·17	1·37	0·36	2·65	0·21	Na_2O
CaO	1·17	0·69	0·40	1·01	3·48	CaO
K_2O	5·14	7·94	8·68	2·71	2·48	K_2O
F	(0·10)	0·40	1·96	< 0·05	< 0·05	F
P_2O_5	(0·18)	—	—	—	2·30	P_2O_5
H_2O+	0·84	3·59	2·75	7·96	12·23	H_2O+
H_2O-		0·83	0·54	1·62	5·05	H_2O-
Less 0 for F		0·17	0·83			Less 0 for F
Total		100·13	99·55	99·80	100·11	

1(R) Type 2 granite, Carnmenellis mass (anal. P. K. Ghosh, 1934). MgO for the Bosahan adamellite from the mode and biotite composition; MnO, F and P_2O_5 on Bosahan specimen.
1(M) Muscovite from adamellite, Bosahan. $Li_2O = 0{\cdot}09\%$, $Rb_2O = 0{\cdot}09\%$ and $F = 0{\cdot}40\%$ spectrographically.
1(B) Biotite from adamellite, Bosahan. $Li_2O = 0{\cdot}36\%$, and $Rb_2O = 0{\cdot}40\%$ spectrographically.
1(S) Silt from the disintegrated Bosahan adamellite (below 12 in. from the surface).
1(C) Ca-saturated clay from the disintegrated Bosahan adamellite (below 12 in. from the surface).

2. *Geochemistry of the rock*

The chemical analyses of the S.W. England granites (Brammall and Harwood, 1932) show that the rocks form a coherent group; compared with average compositions for granite-adamellite rocks the ratios Fe^{+3}/Fe^{+2} and K/Na are slightly high. The minor element contents of several S.W. England granites are shown in Table 2 and these are comparable for most elements. Values found for other granitic rocks indicate that the Bosahan adamellite contains above-average amounts of Cr (15 p.p.m.), Li (400 p.p.m.) and Ni (15 p.p.m.) and less than average amounts of Zr (150 p.p.m.) and Ba (110 p.p.m.). Sahama (1945) recorded the relatively high values of Cr (7 p.p.m.) and Ni (8 p.p.m.) for granite from the S. Lapland complex and observed that the Co/Ni ratio, larger for acidic than basic rocks, approached 4. The Bosahan values for Cr and Ni are thus notably

Table 2

	A	*S*	1(*R*)	1(*Or*)	1(*M*)	1(*B*)	1(*T*)	1(*S*)	(*C*)	2(*R*)	3(*R*)	4(*R*)	5(*R*)	6(*R*)	7(*T*)	8(*T*)	9(*T*)	
B^{+3}	0·23	20	275	—	—	—	3·53%	140	160	—	—	—	—		—	—	—	B
Be^{+2}	0·35	10	15	*	*	10	*	*	*	10	10	15	25		*	*	*	Be
Ga^{+3}	0·62	0·5	20	30	80	140	250	15	15	10	10	15	5		150	800	600	Ga
Cr^{+3}	0·63	1	15	1	1	80	15	45	120	3	4	3	1		2	*	8	Cr
V^{+3}	0·74	10	15	*	5	85	10	*	15	20	7	7	*		30	*	25	V
Mo^{+4}	0·70	10	*	*	*	*	*	*	*	*	*	10	*		*	*	*	Mo
Sn^{+4}	0·71	15	45	*	30	15	20	*	*	20	*	25	*		*	*	*	Sn
Li^{+1}	0·68	1	400	80	320	1800	80	90	115	225	130	225	70	Tr	230	380	350	Li
Ni^{+2}	0·69	1	15	*	1	20	8	45	90	3	3	5	*		10	*	10	Ni
Co^{+2}	0·72	5	4	*	*	10	20	5	4	*	*	*	*		*	*	25	Co
Zr^{+4}	0·79	10	150	*	*	150	55	280	130	40	30	25	40	Tr	*	*	*	Zr
Mn^{+2}	0·80	10	400	*	150	5000	100	900	260	150	120	150	150	550	630	> 1000	600	Mn
Yt^{+3}	0·92	15	15	*	*	40	600	25	*	15	10	10	10		*	*	*	Yt
La^{+3}	1·14	40	*	*	*	400	40?	*	*	*	*	*	*		*	*	*	La
Sr^{+2}	1·12	10	80	45	*	220	*	65	220	90	80	50	80	Abs.	*	*	*	Sr
Pb^{+2}	1·20	15	40	35	*	15	*	15	45	15	15	15	20		60	70	65	Pb
Ba^{+2}	1·34	10	110	225	*	120	*	180	500	80	40	45	115	180	10	*	60	Ba
Rb^{+1}	1·47	5	400	400	800	3500	*	230	550	150	150	150	150		*	*	*	Rb
Tl^{+1}	1·47	0·3	3	1·5	5	5	—	—	3	2	1	1	*		—	—	—	Tl
Cs^{+1}	1·67	50	50	*	*	1350	*	*	*	*	*	*	*		*	*	*	Cs
F^{-1}	1·33	300	1000	—	4000	1·96%	—	*	*	—	—	—	—		—	—	—	F

A Ionic radius Å. After Ahrens (1952)
S Sensitivity p.p.m.
1(R) Adamellite, Bosahan, Carnmenellis.
1(Or) Orthoclase from adamellite.
1(M) Muscovite from adamellite.
1(B) Biotite from adamellite.
1(T) Tourmaline from adamellite.
1(S) Silt from the disintegrated Bosahan adamellite (below 12 in. from surface); oven dried basis.
1(C) Ca-saturated clay from the disintegrated Bosahan adamellite (below 12 in. from surface); oven dried basis.
2(R) Granite (s.l.), Gready, St. Austell.
3(R) Granite (s.l.), Caradon, Bodmin Moor.
4(R) Granite (s.l.), N. Kithill.
5(R) Granite (s.l.), W. Chilsworthy.
6(R) Granite (s.l.), Princetown, Dartmoor (anal. Brammall and Harwood, 1932).
7(T) Tourmaline from pegmatite, Meldon, Okehampton.
8(T) Tourmaline from pegmatite, Tresays, N. of St. Austell.
9(T) Tourmaline from topaz fels, St. Mewan.

An asterisk (*) indicates below sensitivity and a dash (—) absence of data.

high whilst the Co/Ni ratio of 0·27 is much smaller than hitherto recorded (Wager and Mitchell, 1951). The adamellite shows signs of pneumatolytic alteration and the high Li values recall the results of Strock (1936) who observed that Li in German granites increased from the average for the unaltered rocks of 180 p.p.m. to 400–690 p.p.m. as the rocks showed increasing signs of pneumatolysis. The low values for Zr and Ba are characteristic of all the S.W. England granites analysed. Zr, principally reflecting the zircon content, is less abundant than in granitic rocks quoted by Tröger (400 p.p.m. (1935)), Nockolds and Mitchell (300 p.p.m. (1948)) and Hevesey and Würstlin (460 p.p.m. (1934)). Ba, known to have an irregular regional distribution, is below the average of 430 p.p.m. for German and 650 p.p.m. for S. Lapland granites (Engelhardt, 1936, Sahama, 1945) and well below the values for the Caledonian granitic rocks which may contain up to 1500–3000 p.p.m. Ba (Nockolds and Mitchell, 1948).

3. *Geochemistry of the minerals*

(*a*) Orthoclase. Table 2 shows the minor element contents of the sericitized orthoclase and the predominance of the lithophil elements Li, Sr, Ba and Rb is evident. The ions Sr^{+2} and Ba^{+2} and, moreover, Pb^{+2} with their superior charge and lower ionic radii to $K^{+'}$ (1·33 Å) readily replace the latter and a substitution of Al for Si in the tetrahedral positions balances the total charges in the crystal. The large ionic radius of $Rb^{+'}$ does not prevent its being accommodated by the orthoclase and with it occurs a smaller amount of $Tl^{+'}$, giving Rb/Tl (at.) = 640 (cf. the lower value of Ahrens (1948)). Li is not usually abundant in orthoclases —as would be expected from the absence of any Y group ions—and Ahrens and Liebenberg (1945) considered 5 p.p.m. to be above average. The content of 80 p.p.m. found here is doubtless due to the Li content of the fine occluded sericite.

(*b*) Muscovite. A chemical analysis of the hand-picked material is shown in Table 1. The SiO_2 value (usually between 45 and 50% in igneous muscovite) is rather high and suggestive of pegmatitic varieties (Jakob, 1929a, 1929b) but the high CaO content can be matched with other analyses of muscovites from two-mica granites (Weyberg, 1912). The muscovite harbours modest amounts of lithophil minor elements (Table 2) but Sr and Ba are below sensitivity (10 p.p.m.) and they were more easily accommodated by the biotite which crystallised partly at the same time as the muscovite. This distribution contrasts with that found by Nockolds and Mitchell (1948) in the adamellite from Moy where the muscovite contained 2000 p.p.m. Ba and 30 p.p.m. Sr and the biotite 2000 p.p.m. Ba and 70 p.p.m. Sr, but the rock itself contained 3000 p.p.m. Ba and 1200 p.p.m. Sr and the environment in which the micas crystallised must have been rich in these elements.

(*c*) Biotite. The biotite analysed (Table 1) contained an occasional flake of chlorite but was free from tourmaline, etc. The summation of the analysis (99·62%) is low and as silica was estimated before the high fluorine content was appreciated, the SiO_2 value is most suspect. The analysis is, nevertheless, close to those obtained for biotite from Dartmoor, especially Saddle Tor (Brammall and Harwood, 1932) and the ratio $Al_2O_3/(MgO + \text{total Fe as FeO})$ indicates its genesis (Nockolds, 1947). Moderate amounts of the elements Be, Ga, Cr, V, Sn,

Li, Ni, Co, Zr, Yt, La, Sr, Pb, Ba, Rb, Tl and Cs occur (Table 2) and none except Ga in unusual quantities. Although Ga generally follows Al quite closely, the Ga content of the biotite is almost double that in the muscovite and the Al/Ga (at.) ratios are in the surprising proportion 3 : 1 ($5{\cdot}4 \times 10^3$ and $1{\cdot}8 \times 10^3$). Sn is less in the biotite than in the muscovite and it seems unlikely that the element existed in the magma substantially as the fluoride SnF_4 (Ottemann, 1941). The Zr detected (150 p.p.m.) is probably located entirely in the zircon crystals contained in the biotite.

Table 3

	1(*M*)	1(*B*)	10(*B*)	15(*H*)	
Si . . .	6·55	5·43	5·26	6·81	Si
Al . . .	1·45	2·57	2·74	1·19	Al
Al . . .	3·53	0·80	1·01	0·37	Al
Ti . . .	0·06	0·25	0·17	0·10	Ti
Fe^{+3} . . .	0·14	0·48	0·45	0·37	Fe^{+3}
Li . . .	0·05	0·22	0·13	—	Li
Mg . . .	0·26	1·33	1·30	2·68	Mg
Fe^{+2} . . .	0·10	2·44	2·43	1·56	Fe^{+2}
Mn^{+2} . . .	0·01	0·08	0·06	0·08	Mn^{+2}
Na . . .	0·35	0·11	0·11	0·33	Na
Ca . . .	0·10	0·07	0·06	1·93	Ca
K . . .	1·36	1·71	1·80	0·02	K
Rb . . .	0·02	0·04	—	—	Rb
OH . . .	3·19	2·85	3·51	1·76	OH
F . . .	0·17	0·96	0·45	< 0·01	F
(OH + F) .	3·36	3·81	3·96	1·76	(OH + F)
Y group .	4·15	5·60	5·55	5·16	Y group
X group .	1·83	1·93	1·97	2·28	X group

1(M) Muscovite from Bosahan adamellite.
1(B) Biotite from Bosahan adamellite.
10(B) Biotite from Saddle Tor granite, Dartmoor (anal. Brammall and Harwood (1932)).
15(H) Horneblende from Lower Relowas hornblende-schist; see Table 6.
Formulae calculated on basis O + OH + F = 24 and tetrahedral Si + Al = 8.

(*d*) Tourmaline. Spectrochemical estimation of B gave the content as 3·53% B which lies in the restricted range for the mineral group. The minor elements in the Y group include moderately low Li but high Ga (Table 2). Assuming Al_2O_3 to be approximately 30%, the Al/Ga (at.) ratio would be $1{\cdot}65 \times 10^3$, a figure comparable with that for the biotite. None of the tourmaline in thin section occluded zircon and the small Zr content is thus present in the tourmaline lattice. Yt in the X group is high at 600 p.p.m. and like Zr is rare in tourmalines (Carobbi and Pieruccini, 1947; Goldschmidt and Peters, 1931; Ottemann, 1941; Warner, 1935), and neither of these elements was found in three other Cornish tourmalines from pegmatite and topaz-fels.

4. *Weathering of the micas*

(*a*) Muscovite. X-ray analysis of the fresh muscovite showed (002n) and (060) reflections corresponding to $c_0 = 20{\cdot}0$ kX and $b_0 = 8{\cdot}98$ kX respectively and small colourless mica flakes isolated from the soil gave (visually) identical patterns. Although structural changes are thus not drastic, chemical changes are marked and a spectrochemical analysis of small bulk samples of similar flakes from the soil showed a K_2O percentage of less than 8 whilst the loss on ignition for the weathered material substantially exceeded that for the fresh material. The intersheet ions (X group) are thus probably replaced by H_3O^+, but the substitution is never so drastic as to be complete in the single crystals studied by x-rays since on heating there is no collapse of the cell in the c-direction. The minor elements in fresh and soil muscovite were not significantly different in concentration except, possibly, for Rb and F which were both less in the weathered material.

(*b*) Biotite. The fresh biotite gave an x-ray pattern with strong (001) reflections and a (060) reflection corresponding to $c_0 = 9{\cdot}95$ kX and $b_0 = 9{\cdot}19$ kX respectively. Photographs of light yellow-brown weathered flakes (suitably oriented) exhibited diffuse diffraction lines and those at 10 kX and 14 kX were invariably blurred towards each other to form a continuous band sometimes with one or more intensity peaks corresponding to irrational kX unit spacings. After heating these flakes at 550°C for several hours and re-photographing, all spacings above a strong 10 kX reflection disappeared. The weathered flakes are thus mixtures of biotite, biotite-vermiculite mixed layer material (Alexander *et al.*, 1939; Gruner, 1934) with both random distribution and segregation into definite zones (MacEwan, 1949) and vermiculite. Chemical analysis confirmed the reduced K_2O content (around 3·5%) for the light yellow-brown flakes; that this K content may fall substantially below that in weathered muscovite or dioctahedral illites is due to the oxidation of the (octahedrally co-ordinated) Fe^{+2} to Fe^{+3} thereby decreasing the hold of the main lattice on the inter-sheet K positions and allowing the gap between the sheets to increase considerably in individual unit cells. Loss of F on weathering is even more marked than loss of K; a spectrographic test showed less than 0·05% F in the light yellow-brown flakes. Since the octahedral Fe positions are vulnerable, it is only to be expected that the adjacent (OH, F) positions are also, F^- being replaced by $(OH)^-$. The minor elements La, Rb, and Cs, replacing K in the fresh mica, are two-thirds lost on weathering, but the moderate amounts of Sr, Pb and Ba are largely retained. Li is reduced from 1800 p.p.m. to 800 p.p.m. but the other octahedrally co-ordinated minor elements show similar concentrations in fresh and weathered material.

The changes described for the Bosahan biotite are reminiscent of those undergone by (i) the Glen Buchat biotite present in hypersthene-gabbro which gave a final weathering product of relatively pure vermiculite (Walker, 1949) (ii) the Shap adamellite biotite (Wager, 1944) and (iii) the Laitila rapakiwi brown mica (Eskola, 1949) which both lost conspicuous amounts of K. Goethite was recorded as a weathering product of the Glen Buchat and Shap biotites, but no iron mineral was observed associated with the weathered Bosahan biotite.

5. *Mineralogy of the clay*

X-ray examination of the clay from which free Fe oxides had been removed showed the presence of the following minerals with approximate (visual) estimates of their percentages, which are compatible with the K_2O content of 2·48% (Table 1): (i) illite (35%), (ii) vermiculite, (iii) mica intermediate (35% together with the vermiculite), (iv) kaolin (15%), (v) chlorite (5%), (vi) quartz (2–5%) and (vii) feldspar (2–5%). Illite represents original muscovite and hydrothermal sericite whilst the vermiculite and mica intermediate are purely products of the biotite; kaolin is derived from the feldspars but some may, possibly, have come from the vermiculite; chlorite and quartz represent these minerals in the parent adamellite.

The mineralogical composition of a clay derived from the weathering of granitic rock depends much on climatic factors and maturity, etc. Thus Hosking (1940) in studying several mature Australian soils found kaolin to be the characteristic clay mineral under rainfall conditions ranging from 7 in. to 38 in. and illite and vermiculites were invariably absent. Similarly, Alexander *et al.* (1939) found kaolin without illite or vermiculite in the clays from the red podzolic Cecil series but Kelley *et al.* (1939), on the other hand, discovered illite in the youthful Hanford soils and Stephen (1952) in a weathering study of mica-poor granite from the Malverns concluded that kaolin, illite and vermiculite were formed at the seat of the weathering. The mineralogy of the Bosahan clay conforms with the view that the presence of illite in soil clays derived from granitic rocks suggests profile immaturity and the occurrence of vermiculite implies both youthfulness and the presence of a ferromagnesian mineral other than muscovite in the parent rock.

6. *Chemical changes on weathering*

Tables 1 and 2 show the major and minor element composition respectively of the adamellite and the silt and clay derived therefrom. The concentration changes in the process rock → clay on an Al-constant basis include a marked loss of Na (arising from the low plagioclase content of the clay) and a smaller loss of Si. K is decreased less than Na due to its retention as illite or altered biotite in the clay and it is seen that the ratio K/Rb (at.) of 81 for the clay is nearer to those for biotite (45) and muscovite (80) than orthoclase (180). The concentration of Mg and Ti in the clay taken in conjunction with its content of mica intermediate plus vermiculite (35%) suggests that these elements are not removed from the biotite on weathering. It is also seen that the Mg/Ni ratio is preserved on weathering. The P content of the clay shows a considerable increase over that in the rock. The P released from the readily weathered apatite (Mickelson, 1946) was probably fixed (as PO_4 ions) by the free iron oxide forming from the nearby biotite although it may have replaced Si^{+4} (as P^{+5}) in the silicate lattice. The high CaO content of the clay is due partly to the cation exchange capacity of 16 m eqs/100 gms (0·9% CaO) and to the P content of the natural clay; addition of $CaCl_2$ for flocculation presumably formed on insoluble Ca phosphate.

Calculating again on an Al-constant basis, the minor elements Ba, Ga, V, Sn, Li, Co, Zr, Mn, Yt, La, Pb, Rb, Cs, F and B decrease whilst Cr, Ni, Sr, Ba, and Tl increase in the change rock → clay. The drop in Li, Mn, La, Rb, Cs and F

demonstrates their loss principally from the biotite lattice and muscovite lattice (Rb) on weathering; the loss of Li contrasts with the retention of Mg and Ni in the clay and shows the ready solubility of lattice-removed Li. Mn shows a superficial loss since it may on oxidation give silt sized particles of dendritic oxide and is more prominent in the silt than clay. The ratio Al/Ga (at.) changes from 10×10^3 in the rock to 24×10^3 in the clay, suggesting that Ga here breaks its close adherence to Al on weathering. Enhanced values for Ba and Sr in the clay are partly due to contamination from the $CaCl_2$ used in preparing the clay; weathered biotite flakes carried no more of the elements than did the fresh biotite but with decreasing size the altered biotite could readily fix Ba and Sr which would be released from the feldspars by weathering.

The composition of the silt is almost entirely intermediate between that of the rock and clay for the major elements (except for Ca and Mn) and largely so for the minor elements. Zr at 280 p.p.m. in the silt is reduced only to 180 p.p.m. in the clay and rather than suppose the latter value to be due to zircon of e.s.d. below $1{\cdot}3\mu$, it is suggested that the Zr is present as an amorphous metamict product derived from the radio-active zircon. The content of B in the clay slightly exceeds that in the silt and it is clear that a boron-containing mineral capable of being chemically weathered is present in the parent rock; tourmaline, however, was the only boron mineral seen in the numerous thin sections.

Granodiorite-Gneiss

1. *Description of the rock*

Within the Lizard Peninsula occur isolated outcrops of "granite"-gneiss which intrude the serpentine, the gabbro and its associated black dykes but whose relation to the post-Hercynian granite masses of S.W. England is obscure. Three miles N. of Lizard village at Erisey (Grid. ref. 710180) the gneiss outcrops as a readily friable and much decayed quartz-mica-feldspar rock with elongated brown biotite crystals imparting a clear gneissic structure. The rock consists of approximately 50–60% plagioclase (An 15), 20% quartz, 5–10% biotite, 5–10% orthoclase and the accessory minerals chlorite, sphene and iron ores. The orthoclase-plagioclase ratio shows the rock to be a granodiorite-gneiss. Primary muscovite is absent but sericite is conspicuous as an alteration product of the plagioclase. The main minerals exhibit no unusual microscopic properties; in comparison with the Bosahan biotite, the Erisey biotite is more yellow in thin section and carries no zircon inclusions.

2. *Geochemistry of the rock*

A major element analysis of the rotted granodiorite-gneiss (Table 4) shows affinities with analyses of tonalitic rather than granodioritic rocks and in particular the potash content is low at 1·46% K_2O and K/Na (at.) is 0·22 (cf. 0·24 for tonalites and 0·53 for granodiorites).

The minor element concentrations, Table 5, present an interesting comparison with those for the Bosahan adamellite. Li (40 p.p.m.), Rb (85 p.p.m.), and Pb (10 p.p.m.) are respectively 10, 5 and 4 times lower and Ba (270 p.p.m.)

Table 4

	11(*R*)	11(*B*)	11(*WB*)	12(*R*)	13(*C*)	
SiO_2	65·37			50·69	37·59	SiO_2
Al_2O_3	17·57			20·56	26·40	Al_2O_3
TiO_2				0·42	0·40	TiO_2
Fe_2O_3	2·18			1·55	10·87	Fe_2O_3
MgO	1·57			6·84	2·66	MgO
FeO	2·53			3·10	n.d.	FeO
MnO	0·05			0·16	0·20	MnO
Na_2O	4·38	1·76	0·52	3·36	0·58	Na_2O
CaO	1·44			11·99	1·93	CaO
K_2O	1·46	7·53	3·42	n.f.	0·50	K_2O
H_2O+	3·37	3·51		0·94	11·84	H_2O+
H_2O-		1·49	1·56	0·18	6·77	H_2O-
Ignition loss			10·00			Ignition loss
Total	99·92			100·05	99·74	Total

11(R) Rotted granodiorite-gneiss, Erisey, Lizard.
11(B) Fresh biotite from granodiorite-gneiss.
11(WB) Weathered biotite from granodiorite-gneiss.
12(R) Olivine-gabbro, near Coverack, Lizard (anal. Radley (Flett and Hill, 1946)).
13(C) Ca-saturated clay from disintegrated gabbro, Treskewes, W. of St. Keverne, Lizard.

Table 5

	S	11(*R*)	11(*B*)	11(*S*)	11(*C*)	14(*R*)	14(*H*)	13(*C*)	
Ga	0·5	30	60	25	25	25	5	25	Ga
Cr	1	20	100	45	70	100	120	390	Cr
V	10	30	215	40	45	130	220	300	V
Sn	15	*	*	*	30	*	*	15	Sn
Li	1	40	500	80	75	5	5	20	Li
Ni	1	20	20	80	130	150	170	250	Ni
Co	5	10	300	20	35	25	45	80	Co
Zr	10	110	25	250	25	20	40	30	Zr
Mn	10	220	> ½%	500	800	250	—	1500	Mn
Yt	15	25	*	25	40	15	25	140	Yt
La	40	*	*	25?	50	*	50	*	La
Sr	10	70	*	45	75	60	15	10	Sr
Pb	15	10	*	45	75	*	*	50	Pb
Ba	10	270	*	45	45	*	*	240	Ba
Rb	5	85	1800	50	50	*	*	*	Rb

S = Sensitivity in p.p.m.
11(R) Rotted granodiorite-gneiss, Erisey, Lizard.
11(B) Fresh biotite from granodiorite-gneiss.
11(S) Silt from disintegrated granodiorite-gneiss; oven dried basis.
11(C) Ca-saturated clay from disintegrated granodiorite-gneiss; oven dried basis.
14(R) Gabbro, Dean Point, Lizard.
14(H) Hornblende from Dean Point gabbro.
13(C) Ca-saturated clay from disintegrated gabbro, Treskewes W. of St. Kerverne, Lizard; oven dried basis.

twice as high as in the adamellite although the K/Rb and K/Pb ratios are unchanged. Sr is similar in the adamellite and granodiorite-gneiss and the increased Ba in the latter, despite its higher modal plagioclase, suggests that the magma forming the Erisey rock was distinctly richer in Ba. Values for Cr, V, Ni and Co run high compared with average granitic rocks and approach values recorded for diorites; the ratio Co/Ni (0·5) is more normal than that recorded for the adamellite.

3. *Geochemistry of the biotite*

Biotite was partially analysed (Table 4) and the alkali values and x-ray data showed it to be fresh. Spectrographic determinations (Table 5) revealed the high Rb content, giving K/Rb (at.) 75 (higher than that for the adamellite biotite), and the absence of other X-groups ions—surprising in view of the 1·76 Na_2O percentage. In the Y group the absence of Sn is notable but the quantities of Cr (100 p.p.m.), V (215 p.p.m.) and Ni (20 p.p.m.) occasion no surprise. Co, however, is rather high (300 p.p.m.) and it may be following Mg (Sandell and Goldich, 1943), which must be high, judging from the rock analysis and its mode. Fluorine was not detected (below 300 p.p.m.) and this is understandable when the value of H_2O+ is considered, but in view of the high H_2O- figure it is possible it may have been present in the perfectly fresh biotite.

4. *Weathering of the biotite*

The weathering of the biotite from the gneiss is chemically similar to that from the adamellite; the loss of K and Na is conspicuous as is that of Rb and (octahedrally co-ordinated) Li and there is the anticipated rise in H_2O+ judged from the loss on ignition. X-ray photographs of weathered biotite flakes showed a diffuse band between spacings corresponding to 10 and 14 kX units (for first order spacings) with peaks at 10 kX, 14 kX and sometimes intermediately. The presence of a (i.a.) 7 kX reflection established chlorite as a weathering product and the spacings between 10 and 14 kX may accordingly be attributed to biotite-chlorite or biotite-vermiculite mixed layer material. It is not clear why the Erisey biotite weathers to chlorite and the Bosahan biotite to vermiculite without chlorite, but it seems likely that the Mg content of the mica may be an influencing factor. Goethite is an accessory product of weathering.

5. *Mineralogy of the clay*

The clay consists principally of illite (40%), kaolin (40%) and vermiculite (10%). Chlorite is absent and may be assumed to have weathered to vermiculite as has the biotite-chlorite or biotite-vermiculite mixed layer material present in flakes of the weathered biotite. The illite, whose content in the clay is quite high, owes its origin to the feldspars which are sericitised in the immediate parent material; kaolin is the weathering product of plagioclase and probably orthoclase. Quartz and feldspar occur as accessories up to 2 or 3% each and the components of the clay are thus identical to those found in that from the Bosahan adamellite.

6. *Chemical changes on weathering*

The major elements were not determined for the silt or clay but the concentrations found for some of the minor elements in the clay (Table 5) may give an indication

of some of the major element changes in the process rock → clay; in particular the values of Li, Ni and Co in the clay probably reflect its higher Mg and Fe content. Zr (probably exclusively as zircon) is lower in the clay than in the rock but shows a sharp increase in the silt. Ba (expected to be held by the orthoclase) is low in both the clay and silt and its loss from the rock on weathering is indicated.

Hornblende-Gabbro

1. *Description of the rock*

The St. Keverne gabbro forms a small outcrop in the S.E. corner of the Lizard peninsula and is everywhere slightly metamorphosed, secondary hornblende having formed at the expense of the original ferromagnesian minerals; in the quarry at Dean Point (Grid ref. 185204) the rock consists of approximately 40–45% zoned and fairly fresh plagioclase averaging An_{60}, 35–40% amphibole which may be pleochroic with X = green, Y = light green, Z = blue green or, less often, colourless (especially when bordering pyroxene) and 15–20% monoclinic pyroxene; the accessory minerals include olivine, iron ore and apatite (rare).

No locality was found where fresh gabbro supported a residual soil and samples of weathered material from which clay was separated were taken at Treskewes (Grid ref. 784206); the feldspar of the underlying rock was heavily kaolinised but the other minerals resembled those found in the Dean Point specimen.

2. *Geochemistry of the rock and its minerals*

The chemical composition of the Dean Point gabbro is probably similar to that of the Coverack olivine-gabbro (except for Mg) quoted in Table 4. None of the minor elements (Table 5) is present in unusual amounts for gabbros but Sr at 60 p.p.m. is below the average (cf. values of Noll (1934), 170 p.p.m., Hevesey and Würstlin (1934), 140 p.p.m., and Sahama (1945) 80–170 p.p.m. and the ratio (but not the absolute amounts) of Ni to Co is rather high at 6·0 (cf. 3–5 for the olivine-gabbro of Skaergaard (Wager and Mitchell, 1951)). Some of the concentrations of the minor elements in the hornblende (Table 5) suggest its secondary nature. Ga is low, indicating an Al-poor amphibole (i.e. secondary) and Ba and Sr are low compared with values around 150–200 p.p.m. for primary hornblendes (Gottfried, 1929; Hutton, 1944). The low F, here less than 500 p.p.m., also may be more usual in secondary than in igneous hornblendes (Deer, 1938).

3. *Mineralogy of the clay*

The clay consists of approximately 75% fine grained kaolin, 10% illite and 10% chlorite with hornblende (5–10%) and feldspar (3%) as accessories. Fe oxides were removed prior to estimation; no pyroxene was found in the clay. The illite content is compatible with the 0·50% K_2O in the clay; the K may have been supplied by breakdown of the hornblende. The chlorite is probably formed at the expense of the hornblende (see the section on hornblende-schist later), the change requiring an increase of Mg and decrease of Fe^{+2} relative to Si; the value of 2·7% MgO for the clay gives an indication of the high MgO content of the

chlorite compared with that of the hornblende. The fate of parent pyroxene is uncertain; it may, like the hornblende, supply Mg for the formation of the chlorite and Fe for the formation of free iron oxides.

The CaO content of the clay (1·93%) is a reflection of the hornblende and feldspar contents (contribution 0·6–1·2 and 0·36% CaO respectively) and the cation exchange capacity of 12 m eqs/100 gms (equivalent to 0·67% CaO in the clay). The P content is low and can scarcely fix substantial Ca (p. 8).

4. *Chemical changes on weathering*

On the basis of $Al_2O_3 = 100$, the decrease of Si, Fe^{+2} and Na and the increase of H_2O in the change Coverack rock → Treskewes silt → Trewskewes clay compares with data for the adamellite changes. Ca is lost on weathering (due to decomposition of feldspar and lack of P in the clay) but the decrease of Mg from rock through silt to clay is a result of the relative immunity to weathering of the hornblende compared with the feldspars.

The minor elements Cr, V, Li, Co, Yt, Rb and Ba are enhanced and Ni, Zr and Sr decreased in the Treskewes clay compared with the Dean Point gabbro. The factor of change for most elements is two or less assuming a close relationship between the Dean Point gabbro and the parent rock to the Treskewes clay. Ba is much concentrated in the clay and Sr is rejected but it is not clear what causes this selectivity.

Hornblende-Schist

1. *Description of the rock*

Numerous outcrops of hornblende schist occur in the Peninsula and at Lower Relowas (Grid ref. 732227) the rock is preserved as a primary banded schist and consists of approximately 50–60% fresh hornblende, showing the pleochroism X = yellow, Y = grass green and Z = blue green, and 30–40% plagioclase, which is commonly altered to "sericite," but when fresh shows the composition An_{60}. Accessories include sphene (the most common), epidote, clinozoisite, chlorite and iron ore; veins largely of prehnite cut the rock transverse to the schistosity but they are not very common.

2. *Geochemistry of the rock and hornblende*

The chemical composition of the schist (Table 6) is not very different from that of the hornblende-gabbro but the minor element concentration differences are more marked (Tables 5 and 7) and generally higher in the schist although they are of the order expected from gabbros (e.g. Goldschmidt, 1937; Sahama, 1945; Sandell and Goldich, 1943; Tröger, 1935); in particular, Sr is at 200 p.p.m.

The hornblende shows sufficiently high Al_2O_3 (9%; Table 6) to suggest a primary origin and the 12% FeO and ratio of $(Fe^{+2} + Fe^{+3})/Mg^{+2}$ might substantiate this view; on the other hand the low K_2O (and F) is more typical of secondary hornblendes. The minor element contents show only La among the X group ions to be appreciable (200 p.p.m.); in the Y and Z group Ga is now 50 p.p.m. (this compares with the presence of 50 p.p.m. La and 5 p.p.m. Ga in the secondary hornblende from the gabbro).

Table 6

	15(*R*)	15(H)	15(*S*)	15(*C*)	16(*R*)	17(*S*)	17(*C*)	
SiO_2	48·64	45·97	53·22	31·42	40·87	50·51	43·50	SiO_2
Al_2O_3	14·99	9·01	15·73	24·43	3·93	9·89	10·08	Al_2O_3
Cr_2O_3					0·25	0·18	0·04	Cr_2O_3
TiO_2	1·90	0·87	1·49	0·93	0·16	0·65	0·24	TiO_2
Fe_2O_3	3·42	3·42	7·31	18·09	6·17	16·03	22·34	Fe_2O_3
MgO	7·76	12·10	5·14	3·47	32·86	7·13	4·63	MgO
FeO	7·76	12·67	3·50	0·84	2·37	n.d.	n.d.	FeO
MnO	0·30	0·65	0·19	0·26	0·29	0·50	0·30	MnO
Na_2O	3·52	1·12	1·31	0·45	0·39	0·65	0·12	Na_2O
CaO	9·60	12·22	4·64	1·12	2·36	1·51	0·44	CaO
K_2O	0·52	0·05	1·22	0·88	0·04	0·59	0·67	K_2O
H_2O+	1·25	1·78	5·31	11·63	8·95	5·93	7·42	H_2O+
H_2O-	0·10	0·09	1·09	6·23	1·09	6·15	10·30	H_2O-
F	—	< 0·03	—	—	—	—	—	F
Total	100·21	99·95	100·15	99·75	100·09	99·72	100·08	

15(R) Hornblende-schist, Lower Relowas, Lizard (anal. Radley (Flett and Hill, 1946)); total includes $P_2O_5 = 0{\cdot}16\%$ and $CO_2 = 0{\cdot}23\%$.
15(H) Hornblende from Lower Relowas schist.
15(S) Silt from the disintegrated Lower Relowas hornblende-schist (below 14 in. from the surface).
15(C) Ca-saturated clay from the disintegrated Lower Relowas hornblende-schist (below 14 in. from the surface).
16(R) Tremolite-serpentine, W. Kynance Cove (anal. Radley (Flett and Hill, 1946)).
17(S) Silt from the disintegrated tremolite-serpentine, Countybridge, Lizard (below 29 in. from the surface). Cr spectrographically.
17(C) Ca-saturated clay, from the disintegrated tremolite-serpentine, Countybridge, Lizard (below 29 in. from the surface). Cr spectrographically.

A contrast is provided by the hornblendes from the Garabal Hill complex (Nockolds and Mitchell, 1948). Their chemical analyses are similar to that of the hornblende from the schist except for their high Na and Ti but, concerning the minor elements, Ba and Sr average 60 p.p.m. and 120 p.p.m. respectively in the *X* group. Gottfried (1929) and Hutton (1934) found approximately 200 p.p.m. Ba and Sr in primary hornblendes but it is evident that these high values reflect the higher contents of Ba and Sr in the magma from which the hornblende crystallised. Accordingly low values of Ba and Sr in hornblendes may be characteristic of secondary hornblendes or those that have crystallised from a magma not particularly rich in Ba and Sr (e.g., containing less than 700–800 p.p.m. Sr).

3. *Mineralogy of the clay*

The predominant minerals in the clay (excluding free Fe oxides) are chlorite (35%) and kaolin (35%); illite is substantial at 25% whilst hornblende (<5%), vermiculite (<5%) and quartz (2–3%) occur as accessories. Some of the chlorite may have been derived from the small percentage of chlorite in the rock but decomposition of the hornblende must account for most of it. Weathering of the chlorite has produced a small amount of vermiculite by removal of Mg

Table 7

	S	15(*R*)	15(*H*)	15(*S*)	15(*C*)	17(*R*)	17(*S*)	17(*C*)	
Ga . .	0·5	40	50	35	40	*	10	20	Ga
Cr . .	1	20	500	190	180	2800	1200	400	Cr
V . .	10	500	200	190	220	40	85	40	V
Li . .	1	20	—	90	85	*	50	15	Li
Ni . .	1	90	100	170	175	1500	660	660	Ni
Co . .	5	90	70	35	60	200	45	10	Co
Zr . .	10	300	20	330	120	*	95	15	Zr
Mn . .	10	1500	5000	1150	2200	3000	5000	3000	Mn
Yt . .	15	50	—	25	30	*	*	*	Yt
La . .	40	*	200	*	*	*	*	*	La
Sr . .	10	200	—	200	280	10	95	20	Sr
Pb . .	15	*	—	35	70	*	30	10	Pb
Ba . .	10	*	—	190	500	*	220	—	Ba
Rb . .	5	*	—	120	70	*	120	30	Rb

S Sensitivity p.p.m.
15(R) Hornblende-schist Lower Relowas, Lizard.
15(H) Hornblende from Lower Relowas schist.
15(S) Silt from the disintegrated Lower Relowas hornblende-schist (below 14 in. from the surface); oven dried basis.
15(C) Ca-saturated clay from the disintegrated Lower Relowas hornblende-schist (below 14 in. from the surface); oven dried basis.
17(R) Tremolite-serpentine, Countybridge, Lizard.
17(S) Silt derived from the disintegrated Countybridge serpentine (below 29 in. from the surface); oven dried basis.
17(C) Ca-saturated clay derived from the disintegrated Countybridge serpentine (below 29 in. from the surface); oven dried basis.

(compare the alteration of the biotite from the granodiorite-gneiss) as represented schematically by the following—

↑	"Brucite layer"	6 (OH) 6 Mg 6 (OH)	H_2O and Mg^{vi} hydrated
	14 kX		
	"Talc layer"	6 O 4 Si (Al) 4 O + 2 (OH) →	6 O 4 Si (Al) 4 O + 2 (OH)
		6 Mg, Fe^{+2}, Fe^{+3}	6 Mg, Fe^{+2}, Fe^{+3}
		4 O + 2 (OH) 4 Si (Al) 6 O	4 O + 2 (OH) 4 Si (Al) 6 O
↓		Chlorite	Vermiculite

The "brucite layer" (considering this as part of the chlorite) thus breaks down due to hydration and loss of Mg and the remaining Mg in this position hydrates and becomes exchangeable. Alternatively there may be an exchange $2H^{+} \rightleftharpoons Mg^{+2}$ Kaolin is again a weathering product of plagioclase as is the illite. The latter may be overestimated (at 25%) in the clay since K_2O in the clay is below 0·9%.

4. *Chemical changes on weathering*

Assuming Al_2O_3 constant, the losses in the change rock → clay through silt include Ti, Mg, Fe^{+2}, Na and Ca and the gains include Fe^{+3}, H_2O+ and H_2O- (Table 6); except for Ti these resemble the weathering changes of the gabbro. The values of SiO_2 and K_2O for the silt are not intermediate between those for the rock and clay and the presence of quartz in the silt and Rb in the silt and clay (Table 7) but not in the rock indicates some extraneous contamination. The ratio Mg/Ni (at.) in rock, silt and clay is 1300, 440 and 330 respectively; this preferential loss of Mg relative to Ni contrasts with data for the adamellite changes where much smaller amounts of Mg and Ni were contained in the biotite than are present in the hornblende from the schist.

Serpentine

1. *Description of the rock*

The serpentines of the Lizard can be divided mineralogically according to the relative amounts of the minerals enstatite, tremolite and olivine; at Countybridge (Grid ref. 721221) the rock is a tremolite-serpentine and x-ray study and thin sections show it to consist of chrysotile and antigorite (together totalling approx. 60–70%), chlorite (10–15%), and tremolite (5–10%) with magnetite, chromite, olivine, enstatite, and feldspar as accessories.

2. *Geochemistry of the rock*

The composition of the tremolite-serpentine from Kynance after Radley (Flett and Hill, 1946) is given in Table 6 and that of the Countybridge specimen would probably be very similar. Detectable minor elements in the Countybridge rock are few and only Cr, Ni and Co (and Mn) are prominent (Table 7). The chromite accounts for most of the chromium in the rock (2800 p.p.m.) but the silicates chlorite and olivine more than the iron spinel magnetite harbour the Ni and Co (1500 p.p.m. and 200 p.p.m. respectively). The ratio Ni/Co (at.) of 7·5 and the concentrations of Cr, Ni and Co are typical for periodites and serpentines (Bishopp, 1946; Fenoglio, 1948; 1949–50; Goldschmidt, 1937; Pieruccini, 1946; Sahama, 1945). Radley recorded a trace of V in the Lizard serpentines and here 40 p.p.m. V was found; the element is probably substituting as V^{+5} for Fe^{+3} in the magnetite lattice.

3. *Mineralogy of the clay*

The clay (excluding free Fe oxides) consists principally of chlorite (approx. 70%), illite (15%) and kaolin (5%). The occurrence of montmorillonoid (5%) and talc (5%), however, distinguishes this clay from the other Cornish ones previously described. The analysis of the clay (Table 6) shows a fairly high SiO_2 content (44%) and values for Al_2O_3, MgO and K_2O of 10%, 4·6% and 0·67% respectively. An assumption of 15% illite and 5% talc disposes of the potash and most of the alumina implying a chlorite plus montmorillonoid composition of not less than 4% Al_2O_3 and 4·3% MgO (depending on the free Fe oxides content). The original chlorite of the rock has doubtless contributed to the chlorite in the clay (without

structural change but permissible chemical change) and it is likely that the chrysotile and antigorite, destroyed in the course of weathering, supplied some of their Mg and (relatively) more of their Si towards chlorite synthesis; excess Mg may have formed talc (which was not identeifid with certainty in the parent material). Feldspar gave rise to kaolin but it is unlikely that any of the rock constituents contained sufficient K to produce illite and the presence of the latter is due to contamination.

The production of montmorillonoid is not difficult to visualise since the structural skeletons of it and chlorite are similar. The "talc layer" of chlorite (considering it as an alternation of talc and brucite layers) exerts a negative charge of 2 per unit cell which is balanced by that of the "brucite layer." Substitution (including oxidation) with or without ion removal in the "talk positions" of the chlorite may lead to a diminished negative charge and a consequent weakening of the hold on the "brucite layer"; if the charge drops to between 1 and 0·6 per unit cell, swelling can occur between successive "talk layers" (due, for example, to the adsorption of a double molecular layer of glycerol) and the mineral is effectively a montmorillonoid.*

The parent material of soil clays containing montmorillonoid are predominantly basic or rich in Mg, e.g. serpentine (Kelley, 1939), basalts (Hosking, 1940; Muir, 1951), hornblende-granite (Nagelschmidt *et al.*, 1940), glauconitic sandstone (Cole, 1943) and calcareous marl (Coleman and Jackson, 1945), and impeded drainage is usually a condition for montmorillonoid formation.

The weathering products of chlorite in Cornish soils are decided, in part, by drainage; vermiculite is a product in well-drained soils and montmorillonoid a product in the very poorly-drained soil overlying the serpentine.

4. *Chemical changes on weathering*

The expected losses of Si, Mg and Ca and gains of Fe^{+3} and H_2O relative to Al occur on weathering (rock → silt → clay; Table 6). An increase in K is due partly to contamination as is the appearance of substantial Zr (95 p.p.m.) and Li (50 p.p.m.) in the silt. The ratio Mg/Ni again decreases on weathering and compares with data for the gabbro and hornblende-schist. The sharp decrease of Cr from silt and clay is due to the limit of physical weathering and chemical stability of chromite (cf. zircon from the "granite"-gneiss).

Summary of Results and Conclusions

I. *Minerals in the rocks and clays*

Fig. 1 shows the distribution of the eight minerals identified in the clays (after removal of free Fe oxides) derived from the five weathered rocks. Kaolin and illite occur in all the clays and vermiculite occurs in those from the adamellite, granodiorite-gneiss and hornblende-schist. Montmorillonoid and talc, however, are restricted to the clay derived from the serpentine but it is possible that the

* Swelling chlorite (Stephen and MacEwan, 1950, 1951) may also be produced ("talc layer" charge uncertain) but due to the presence of both chlorite and illite this cannot be distinguished from montmorillonoid in the serpentine-derived clay.

Fig. 1. Approximate mineralogical composition of Cornish clays ($<2\mu$) derived from weathering from various rocks. Free Fe oxides removed.

latter mineral may, like feldspar, hornblende and quartz, be a physical product of weathering. Nevertheless the occurrence of talc in a soil clay has not previously been reported.

Under the climatic conditions prevailing in Cornwall, feldspar decomposes to kaolin with or without illite (depending on the availability of K from the feldspar or elsewhere) and muscovite and hydrothermal sericite change, with but slight modification of their structure and composition, to illite. The weathering products of the biotite probably depend on its chemical composition. Biotite from the adamellite, which has a low MgO content, weathers to vermiculite via biotite-vermiculite intermediate mineral; biotite from the granodiorite-gneiss with a higher MgO content, weathers first to chlorite (seen in individual flakes of weathered

biotite) and then to vermiculite (present, without chlorite, in the clay). The suggested role of MgO implies that soil vermiculites are poorer in MgO than soil chlorites but, unfortunately, no analyses for such mineral are known. Hornblende weathers to give chlorite (from the gabbro and hornblende schist) but it is doubtful if it gives rise directly to vermiculite. Pyroxene is only present in the gabbro and then to a modest extent; its weathering fate is uncertain. Chlorite under conditions of open drainage (i.e. above the adamellite and granodiroite-gneiss) changes to vermiculite but under impeded drainage conditions (i.e. above the serpentine) gives rise to montmorillonoid. Chrysotile, present only in the serpentine, disappears on weathering; it releases elements which may reunite to form chlorite.

II. *Chemical composition of the rocks and clays*

The analyses of the Ca-saturated clays derived by weathering from adamellite, gabbro, hornblende-schist and serpentine are shown in Tables 1, 4 and 6 together with analyses of either the parent material or a rock close in composition to that of the parent.

Relative to Al_2O_3, all four rocks lose Si, Fe^{+2}, Mn and Na and gain Fe^{+3} and $H_2O\pm$ on weathering. Adamellite is the only rock not losing Ti, Mg and Ca in the change to the clay fraction but Ca in the clay is abnormally high due to the high phosphorus content ($CaCl_2$ in neutral solution was used to floculate the clays) and the concentration of Ti and Mg in the clay is a result of the selective weathering of biotite which contains nearly all the Ti and Mg in the rock. K is readily lost in weathering when its content in the parent material is moderate or higher (e.g. $>2\%$ K) but it is not clear if it is concentrated in the clay of the weathered material when the content in the parent is low (e.g. $<1\%$ K) since the possibility of some extraneous contamination (and introduction of K as illite) cannot be ruled out (e.g. above the hornblende-schist). These described changes are well-known ones for rocks weathering in temperate climates (Correns, 1940; Reiche, 1945).

The compositions of the clays are much nearer to each other than are those of the rocks. Thus the extremes of composition for MgO are 2·8–5·2% for the clays and 0·50–33·0% for the rocks. Similarly, the elements, K, Ca, Ti, Na and Si (in order of decreasing differences of extremes) show less variation in the clays from the weathered material than they do in the parent materials. Chemical changes in the process rock → clay are shown diagrammatically in Fig. 2 where the apices of a triangle are used to denote molecular proportions of the oxides of Si + Al, the oxides of the *Y* group excluding Al and the oxides of the *X* group. The grouping of the points corresponding to rocks is less close than that of the points corresponding to clays, although the marked difference in composition of the clay from the serpentine to those of the other (rather similar) clays is not so clearly demonstrated by this choice of scales.

III. *Minor elements in the Cornish minerals, rocks and clays*

The behaviour of several minor elements in relation to their normal major associates is of interest.

Ga, larger but close to Al in ionic size, (0·62 Å and 0·51 Å) is lost relative to Al in weathering processes. Values for Al/Ga (at.) varying from $5{\cdot}2 \times 10^3$ in the hornblende-schist to $11{\cdot}3 \times 10^3$ in the gabbro are increased in the silts and clays but there is as much spreading of values in the rocks as in the clays. The minerals, by contrast, return lower Al/Ga (at.) values; biotite (from adamellite) and hornblende (from schist) give $1{\cdot}8 \times 10^3$ and $2{\cdot}5 \times 10^3$, muscovite (from adamellite) $5{\cdot}5 \times 10^3$ and orthoclase (also from adamellite) $8{\cdot}4 \times 10^3$.

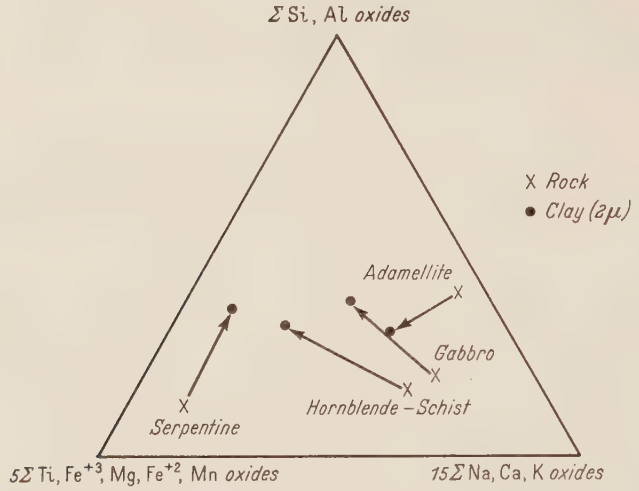

Fig. 2. Chemical composition of Cornish rocks and their 2μ clay weathering products. Molecular proportions of oxides.

Ni frequently follows Mg in the magmatic cycles where sulphides are absent and the Mg/Ni (at.) ratio is not readily correlated with, for example, changing rock acidity. Values for the rock vary from 320 to 1300 and for the clays from 49 to 430; there is invariably a decrease of Mg/Ni for a particular rock weathering to its clay indicating a preferential concentration of Ni. However, the ratio does not tend to a constant on weathering and, indeed, there is wider variation amongst the clay values than amongst the rock ones. The minerals analysed exhibit high Mg/Ni (at.) ratios, indicating relative paucity of Ni. Hornblende from the gabbro gave 1040, hornblende from the schist 1780, biotite and muscovite from the adamellite, 4200 and 19,000.

Co^{+2} and Fe^{+2} have almost identical ionic radii (0·72 and 0·74 Å) but for rocks not genetically connected it is not to be expected that any constancy of Fe^{+2}/Co (at.) is attained. Deductions from Goldschmidt's data indicate that Fe^{+2}/Co (at.) is smaller for basic rocks, ranging from 1000–2000 for granites, syenites, and nepheline-syenites (1–2% FeO) through 800 for gabbros (8% FeO) to 350 for peridotites (10–12% FeO). This tendency is shown by the Cornish rocks (bearing in mind the value of Fe^{+2} in the serpentine is below that for the original magma due to post-magmatic oxidation). For rocks lying on the same line of liquid descent the ratio Mg/Co is more constant than Fe^{+2}/Co (Nockolds and Mitchell, 1948; Sandell, 1943; Wager and Mitchell, 1951, Table F).

In weathering, however, although Fe^{+2} is readily oxidized to Fe^{+3} whereas Co^{+2} will not oxidise to cobaltic compounds (stable only as complex ions), Co does not accompany Mg and the ratios Mg/Co show haphazard trends comparing values for rock and derived silt and clay. Since Co is retained in all the clays and FeO tends to zero, the ratio Fe^{+2}/Co must decrease substantially on weathering. For the adamellite, granodiorite-gneiss, hornblende-schist and serpentine there are regular increases in the values of the ratio Ni/Co for rock → clay, but there is a slight fall in the ratio for gabbro rock → clay.

The elements K and Rb are normally associated with each other but K/Rb (at.) ratios are known to vary widely. Orthoclase from adamellite gives K/Rb (at.) = 810, muscovite and biotite from adamellite 180 and 45 respectively and biotite from the granodiorite-gneiss the value of 75. The adamellite rock ratio of 230 is reduced in the clay to 81 (due to the preferential weathering of biotite) but there is an increase of the K/Rb ratio from silt to clay for the hornblende-schist and serpentine weathering products. The ionic radius of Rb (1·47 Å) exceeds that of K (1·33 Å) significantly and the loss of Rb relative to K on weathering is to be expected.

Summary

The Cornish rocks (i) adamellite, (ii) granodiorite-gneiss, (iii) gabbro, (iv) hornblende-schist and (v) serpentine are described together with their weathering products. The minerals illite and kaolin are present in all the (2μ) clays derived from the rocks by weathering but chlorite and vermiculite are less widespread and talc and montmorillonoid occur in one clay only. Both mineralogically and chemically the compositions of the clays are nearer each other than are those of the rocks. The role of the minor elements in the rocks, minerals and clays in relation to the fate of the major elements is discussed.

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References

Ahrens, L. H.	1945	Trans. geol. Soc. S.Afr. **48**, 207–231
Ahrens, L. H.	1948	J. Geol. **56**, 578–590
Ahrens, L. H.	1952	Geochim. et Cosmochim. Acta **2**, 168
Ahrens, L. H. and Liebenberg, W. R.	1945	Trans. geol. Soc. S.Afr. **48**, 75–82
Alexander, L. T., Hendricks, S. B. and Nelson, R. A.	1939	Soil Sci. **48**, 273–279
Bishopp, D. W.	1946	Sci. Proc. roy. Dublin Soc., n.ser. **24**, 125–133
Brammall, A. and Harwood, H.	1932	Quart. J. geol. Soc. Lond. **88**, 171–237
Carobbi, G. and Pieruccini, R.	1947	Amer. Min. **32**, 121–130
Cole, W. F.	1943	J. roy. Soc. W.Aust. **27**, 229–243
Coleman, R. and Jackson, M.	1945	Proc. Soil Sci. Soc. Amer. **10**, 381–391
Correns, C. W.	1940	Naturwissenschaften **28**, 369–376
Deer, W. A.	1938	Miner. Mag. **25**, 56–74

Engelhardt, W. von	1936	Chem. d. Erde **10**, 187–247
Eskola, P.	1949	Bull. Comm. géol. Finl. No. **144**, 113–116
Fenoglio, M.	1948	Ric. sci. **18**, 801–802
Fenoglio, M.	1949–50	Atti Accad. Torino **84**, 71–73
Flett, J. S. and Hill, R. N.	1946	Mem. geol. Surv. U.K. Geology of Lizard and Meneage 2nd Ed. p. 53, 76 and 88
Ghosh, P. K.	1934	Quart. J. geol. Soc. Lond. **90**, 240–276
Goldschmidt, V. M.	1937	Skr. norske Vidensk Akad. **1** Mat. naturv. Kl. No. 4
Goldschmidt, V. M. and Peters, Cl.	1931	Nachr. Ges. Wiss. Göttingen, Math.-physik Kl., 165–183
Gottfried, C.	1929	Verh. geol. Reichs Anst. (St. Anst.) Wien, 230
Groves, A. W.	1936	Silicate Analysis. Allen and Unwin.
Gruner, J. W.	1934	Amer. Min. **19**, 557–575
Hevesy, G. von and Würstlin, K.	1934	Z. anorg. Chem. **216**, 305–311
Hosking, J. S.	1940	J. Coun. sci. industr. Res. Aust. **13**, 206–216
Hutton, C. O.	1944	Trans. roy. Soc. N.Z. **74**, 125–153
Jakob, J.	1929*a*	Z. Kristallogr. **69**, 511–515
Jakob, J.	1929*b*	Z. Kristallogr. **70**, 493–496
Kelley, W., Dore, W., Woodfold, A. and Brown, S. M.	1939	Soil Sci. **48**, 201–255
Landergren, S.	1945	Ark. Kemi Min. Geol. **19A**, No. 25, 1–7
MacEwan, D. M. C.	1944	Nature, Lond. **154**, 577–578
MacEwan, D. M. C.	1949	J. Soil Sci. **1**, 90–103
Mickelson, G. A.	1946	Ph.D. Thesis, Ohio State University 1942, Abstract of Doctorial Dissertations No. 40 Ohio State Univ. Press
Muir, A.	1951	J. Soil Sci. **2**, 163–182
Nagelschmidt, G.	1941	J. Sci. Instrum. **18**, 100–101
Nagelschmidt, G., Desai, A. and Muir, A.	1940	J. Agri. Sci. **30**, 639–653
Nockolds, S. R.	1947	Amer. J. Sci. **245**, 401–420
Nockolds, S. R. and Mitchell, R. L.	1948	Trans. Roy. Soc. Edinb. **61**, 533–575
Noll, W.	1934	Chem. d. Erde **8**, 507–600
Ottemann, J.	1941	Z. angew. Miner. **3**, 142–169
Pieruccini, R.	1946	Period. Miner. **15**, 147–205
Piper, C. S.	1944	Soil and Plant analysis. Monograph, Waite Agricultural Res. Inst. Adelaide
Reiche, P.	1945	Univ. N. Mex. Publ. Geol. **No. 1**, 87 pp.
Sahama, Th. G.	1945	Bull. géol. Finl. **No. 135**, 5–86
Sandell, E. B. and Goldich, S. S.	1943	J. Geol. **51**, 99–115 and 167–189
Stephen, I.	1952	J. Soil Sci. **3**, 20–33
Stephen, I. and MacEwan, D. M. C.	1950	Géotechnique, Lond. **2**, 82–83
Stephen, I. and MacEwan, D. M. C.	1951	Clay Minerals Bull. **1**, 157–162
Strock, L. W.	1936	Nachr. Ges. Wiss. Göttingen, IV N.F. **1**, No. 15, 171–204
Tröger, E.	1935	Chem. d. Erde **9**, 286–310
Wager, L. R.	1944	Proc. Yorks. geol. (polyt.) Soc. **25**, 366-372
Wager, L. R. and Mitchell, R. L.	1951	Geochim. et Cosmochim. Acta **1**, 129–208
Walker, G. F.	1949	Miner. Mag. **28**, 693–703
Warner, T. W.	1935	Amer. Min. **20**, 531–536
Weyberg, Z.	1912	Neues Jb. Min. Geol. Paläont. I, 398

Geochimica et Cosmochimica Acta, 1953, Vol. 4, pp. 179 to 208. Pergamon Press Ltd., London

Calcium-poor garnet in relation to metamorphism

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ABSTRACT

(1) The writer has carried out a systematic study of pyralspites (calcium-poor garnets) in pelitic metamorphic rocks of the Gosaisyo-Takanuki district. With the increase in metamorphic grade of their host-rocks, the MnO content of the pyralspites decreases, while the FeO content increases. Accompanying the variations in composition, the edge length of the unit cell of the minerals shortens and the refractive index becomes generally higher. The associated biotite also varies in composition and proportion with advancing metamorphism.

(2) The MnO content of pyralspites in ordinary pelitic metamorphic rocks generally decreases with the increase in metamorphic grade. When we use main mineral facies as a scale of metamorphic grade, however, the MnO contents of pyralspites in ordinary pelitic metamorphic rocks of the same mineral facies differ in different districts, owing to the difference in character of metamorphism in different districts. Thus, the MnO contents of pyralspites in ordinary pelitic metamorphic rocks are a useful indicator of the character of metamorphism (Fig. 5).

(3) When we treat pyralspites not only from ordinary pelitic metamorphic rocks, but also from rocks of a much wider range of composition, the minerals show a progressive enlargement of their composition field from Mn-rich compositions to Fe-rich ones, and further to Mg-rich ones, with advancing metamorphism, instead of the above-mentioned gradual decrease in MnO content (Fig. 7).

(4) The progressive enlargement of the composition field in pyralspite with advancing metamorphism can be explained in terms of crystal chemistry. Mn^{+2} ions are the most appropriate in size to enter the crystal structure of pyralspite, and so only pyralspite rich in Mn^{+2} can be formed at very low temperatures. With the increase in the temperature of its formation, ions whose ionic radii are less appropriate to the crystal, such as Fe^{+2} and further Mg^{+2}, become increasingly free to enter the crystal, and so the composition field of pyralspite becomes progressively larger with advancing metamorphism of the host-rocks.

Such crystallo-chemical properties of pyralspite reveal themselves also in the distribution of Mn^{+2}, Fe^{+2}, and Mg^{+2} in pyralspites and associated ferromagnesian minerals.

1. Introduction

According to the studies of Ford [1], Boeke [2], and others, the chemical composition of garnet in metamorphic rocks may usually be represented approximately as consisting of five molecules:

Sp (Spessartine)	$Mn_3Al_2Si_3O_{12}$
Alm (Almandine)	$Fe_3Al_2Si_3O_{12}$
Py (Pyrope)	$Mg_3Al_2Si_3O_{12}$
Gr (Grossularite)	$Ca_3Al_2Si_3O_{12}$
And (Andradite)	$Ca_3Fe_2Si_3O_{12}$

Sp, Alm, and Py molecules are miscible with one another and with small quantities of Gr and And to form one continuous solid solution group, while Gr and And molecules are miscible with each other and with small quantities of Sp, Alm, and Py to form another continuous solid solution group. The two fields of these solid solution groups are separated by a large immiscibility gap. The writer calls garnet of the former group (calcium-poor solid solution) *pyralspite*, and that of the latter group (calcium-rich one) *grandite* after Winchell [3].

In this paper the writer intends to show how the stability relations as well as the modes of occurrence of pyralspites in metamorphic rocks are controlled by

their crystallo-chemical properties. The relation discovered will be useful for a classification of metamorphism.

2. Pyralspites from the Gosaisyo-Takanuki District

(1) *Introductory statement*

The writer has carried out a systematic study of pyralspites in pelitic metamorphic rocks of the Gosaisyo-Takanuki district in Abukuma Plateau, Japan. The Gosaisyo-Takanuki district is a regional-metamorphic area with a width of about 30 km from east to west (36° 55′–37°10′N, 140°30′–50′E). The metamorphic complex of the district is mainly composed of schistose rocks derived from basic, pelitic, and psammitic rocks, with a subordinate quantity of calcium-rich rocks. In the middle part of the district there are two intrusive plutonic masses, called "the Miyamoto composite mass and the Mikabu gabbroic stock" by Gorai [4]. The Miyamoto composite mass is mainly composed of granodioritic and gabbroic rocks. In the west of the district there are two larger plutonic masses, "the Samegawa and the Isikawa composite masses" of Gorai, mainly composed of quartz-dioritic rocks.

(2) *Metamorphism of the Gosaisyo-Takanuki district*

The metamorphic grade of the rocks of this district appears to be closely related to the distribution of the above-mentioned plutonic masses. On the whole it increases progressively towards the west, that is, towards the large plutonic masses in the west of the district. But, in the area adjacent to the west border of the Miyamoto composite mass there is a local increase in metamorphic grade, probably due to the thermal effect of the mass, as will be shown later.

The calcium-rich metamorphic rocks of this district are classified into two groups: (i) limestones and (ii) calcium-rich lenses and bands in metamorphosed basic rocks. As regards them, the writer [5] has divided the district generally from east to west into four progressive metamorphic zones, as follows:

Zone I. This Zone is characterized by the absence of diopside-hedenbergite and grandite garnet in calcium-rich rocks. The temperature of metamorphism was probably too low to form those minerals.

Zone II. This Zone is characterized by the entrance of diopside-hedenbergite and grandite in calcium-rich rocks. The minerals are not confined to the present Zone but persist into the succeeding ones.

Zone III. This Zone is characterized by the disappearance of epidote-clinozoisite, which is abundant in the preceding Zones.

Zone IV. This Zone is characterized by the entrance of wollastonite in rocks of appropriate compositions. This mineral does not occur in the preceding Zones. To this Zone belongs not only the westernmost part of the district, but also the area adjacent to the west border of the Miyamoto composite mass in the middle part.

In Fig. 1 the progressive metamorphic zones for calcium-rich rocks are indicated by roman numerals I–IV. The boundaries between the Zones are shown by lines marked with "15%," "10%," and "5·7%," the meaning of which will be explained

on a later page. Zone I roughly corresponds in metamorphic grade to Eskola's [6] epidote-amphibolite facies, and Zones III and IV to his amphibolite facies.

(3) *Pelitic metamorphic rocks*

The pyralspites described here occur in the pelitic metamorphic rocks of the district. The progressive metamorphism causes a general increase in grain size of the pelitic metamorphic rocks, together with variations in their constituent

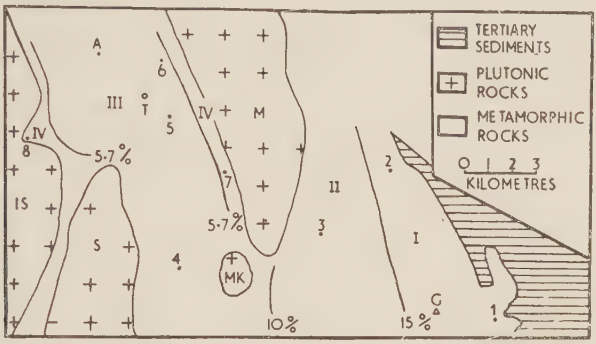

Fig. 1. Geological sketch map of the Gosaisyo-Takanuki district

minerals. The rocks are mainly composed of quartz, feldspar, and biotite, sometimes with varied quantities of white mica, pyralspite, sillimanite, and/or cordierite. The occurrence of pyralspite, sillimanite, and cordierite is too sporadic to delineate a definite series of progressive metamorphic zones, each of which is characterized by a particular index mineral. Andalusite was rarely found in biotite schist from Gosaisyo-Pass and thereabouts in the area of Zone I for calcium-rich rocks. But it is uncertain whether it is a mineral formed by the metamorphism now under consideration.

In all the host-rocks from which the analyzed pyralspites, Nos. 1–8 in Table 2, were separated, the garnet amounts to about 1–8% of the rock by volume, together with much larger quantities of biotite. In Fig. 1, points with Arabic numerals 1–8 and A refer to analysis numbers in Table 2.

(A) In Zone I for calcium-rich rocks, pelitic metamorphic rocks are generally represented by fine-grained biotite schist, sometimes with varied quantities of sericite, chlorite, epidote-clinozoisite, and/or graphite, and rarely with small quantities of pyralspite. Two pyralspites were separated from pelitic metamorphic rocks of this Zone and were analyzed (Analyses Nos. 1 and 2 in Table 2).

Host-rock of the analyzed pyralspite No. 1: Pyralspite-bearing biotite-schist from Negisi, Kadono-mura (Specimen No. AM501028—4a). It is a black fine-grained schist mainly composed of quartz and biotite, with small quantities of acid plagioclase, pyralspite, chlorite, clinozoisite, titanite, apatite, tourmaline, and opaque mineral (mainly graphite). Pyralspite occupies about 1·0% of the rock by volume, and biotite about 23%. Pyralspite tends to occur in idiomorphic crystals up to 0·4 mm in diameter, while the

other minerals occur generally in crystals smaller than 0·1 mm. The biotite is light greenish brown in colour (Z). The chemical composition of this rock is shown in column 1 of Table 1 and in Fig. 2. The graphite content of the rock was not determined, though it may be 1% or more.

Host-rock of the analyzed pyralspite No. 2: Pyralspite-bearing biotite-schist from Nyuzyo, Iritono-mura (Specimen No. AM501020—10b). It is a brown fine-grained schist mainly composed of quartz and biotite, with small quantities of acid plagioclase, pyralspite, sericite, chlorite, clinozoisite, and opaque mineral. Pyralspite occupies about 1·6% of the rock by volume, and biotite about 15%. Pyralspite tends to occur in idiomorphic crystals which measure ordinarily 0·1–0·2 mm in diameter, rarely reaching 0·5 mm, while the other minerals occur in crystals generally smaller than 0·2 mm in diameter. The biotite is brownish yellow in colour, and may have suffered slight secondary alteration, judging from its low K_2O and high H_2O contents.

Table 1. *Chemical composition of pyralspite-bearing pelitic metamorphic rocks of the Gosaisyo-Takanuki district*

	I	II
SiO_2	62·18	63·75
Al_2O_3	14·81	17·10
TiO_2	1·09	0·67
Fe_2O_3	0·78	1·12
FeO	5·58	3·84
MgO	3·42	1·93
MnO	0·41	0·03
CaO	3·61	1·81
Na_2O	1·41	3·37
K_2O	2·02	4·29
H_2O+	2·84	1·25
H_2O-	0·13	0·22
P_2O_5	0·56	0·15
C	n.d.	n.d.
Total	98·84	99·53

I. Pyralspite-bearing biotite schist from Negisi, Kadono-mura (Specimen No. AM501028—4a). This is the host-rock of the analyzed pyralspite No. 1 in Table 2.

II. Sillimanite-pyralspite-bearing muscovite-biotite gneiss from Yokogawa, Miyamoto-mura (Specimen No. AM470802—16). This is the host-rock of the analyzed pyralspite No. 5 in Table 2.

(B) In Zone II for calcium-rich rocks, pelitic metamorphic rocks are generally represented by medium-grained biotite schists, sometimes with varied quantities of muscovite and pyralspite. In the lower-grade part of Zone II the occurrence of pyralspite in pelitic metamorphic rocks is rare, while in the higher-grade part of the Zone it is not infrequent, and the quantity of the mineral becomes sometimes fairly large. A pyralspite was separated from a pelitic metamorphic rock of this Zone and was analyzed (Analysis No. 3 in Table 2).

Host-rock of the analyzed pyralspite No. 3: Pyralspite-biotite schist from between Kaiya and Isizumi, Isizumi-mura (Specimen No. AM470623—3). It is a well-laminated

medium-grained schist mainly composed of quartz, oligoclase, biotite, and pyralspite, with small quantities of muscovite, green hornblende, tourmaline, apatite, and opaque mineral. Pyralspite occupies about 8% of the rock by volume, and biotite about 12%. Pyralspite occurs in grains up to 0·2 mm in diameter, while crystals of the other minerals sometimes reach 1 mm or more in length. The biotite is dark greenish brown in colour.

(C) In Zones III and IV for calcium-rich rocks, pelitic metamorphic rocks are generally represented by coarse-grained biotite gneisses, not infrequently with

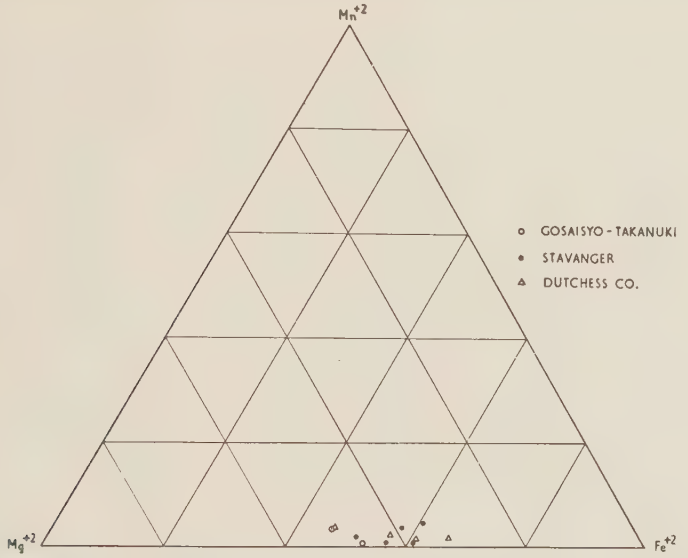

Fig. 2. Atomic proportions of Mn^{+2}, Fe^{+2}, and Mg^{+2} in pyralspite-bearing ordinary pelitic metamorphic rocks

varied quantities of muscovite, pyralspite, sillimanite, and/or cordierite. The quantity of pyralspite present in these rocks is sometimes fairly large. Three pyralspites were separated from ordinary pelitic metamorphic rocks of Zone III and two from those of Zone IV, and were analyzed (Analyses Nos. 4–6 and 7–8 respectively in Table 2).

Host-rock of the analyzed pyralspite No. 4: Pyralspite-bearing biotite gneiss from between Nyudo and Takinotaira (Zone III), Miyamoto-mura (Specimen No. AM491116—1). It is a coarse-grained gneiss mainly composed of quartz, microcline, and biotite, with small quantities of pyralspite and opaque mineral. Pyralspite occupies about 1% of the rock by volume, and biotite about 10%. Most grains of these minerals are 0·5–3·0 mm in diameter. The biotite is deep yellowish brown in colour.

Host-rock of the analyzed pyralspite No. 5: Sillimanite-pyralspite-bearing muscovite-biotite gneiss from Yokogawa (Zone III), Miyamoto-mura (Specimen No. AM470802—16). It is a medium-grained gneiss mainly composed of quartz, plagioclase (An 24%), microcline, biotite, and muscovite, with small quantities of sillimanite, pyralspite, apatite, zircon, and opaque mineral. Pyralspite occupies about 0·01% of the rock by volume, and biotite about 28%. Most grains of these minerals are smaller than 0·3 mm in diameter, though quartz sometimes occurs in large grains reaching 1·0 mm in diameter. The biotite is brown in colour. The determination of MnO content of the pyralspite No. 5 was slightly less precise than those of the others, as only a little of the mineral could be separated. As the pyralspite is present in extremely small amounts and is distributed very unevenly

in the rock, the bulk of the biotite present in the rock is probably not in equilibrium with the pyralspite. The chemical composition of the rock is shown in column II of Table 1 and in Fig. 2.

Host-rock of the analyzed pyralspite No. 6: Sillimanite-bearing pyralspite-biotite gneiss from Tinokubo (Zone III), Miyamoto-mura (Specimen No. AM491104–2). It is a laminated coarse-grained gneiss mainly composed of quartz, oligoclase, and biotite, with small quantities of microcline, pyralspite, sillimanite, zircon, and opaque mineral. Pyralspite occupies about 5% of the rock by volume, and biotite about 18%. Most grains of these minerals are smaller than 2·0 mm in diameter. The biotite is deep yellowish brown in colour.

Host-rock of the analyzed pyralspite No. 7: Sillimanite-pyralspite-bearing biotite-muscovite gneiss from Daibara (Zone IV), Miyamoto-mura (Specimen No. AM491105—2). It is a coarse-grained gneiss mainly composed of quartz, oligoclase, microcline, biotite, and muscovite, with small quantities of pyralspite, sillimanite, zircon, and opaque mineral. Pyralspite occupies about 0·5% of the rock by volume, and biotite about 20%. Most grains of these minerals are smaller than 1·2 mm in diameter, though sillimanite sometimes occurs in large crystals reaching 1·5 mm in length. The biotite is brown in colour.

Host-rock of the analyzed pyralspite No. 8: Pyralspite-bearing biotite gneiss from Hottyuka (Zone IV), Samegawa-mura (Specimen No. AM491115—35). It is a medium-grained gneiss mainly composed of quartz, plagioclase (An 30%), and biotite, with small quantities of pyralspite, apatite, and graphite. Pyralspite occupies about 1% of the rock by volume, and biotite about 12%. Most grains of these minerals are smaller than 0·7 mm in diameter. The biotite is deep yellowish brown in colour.

(D) In addition, another pyralspite (Analysis A in Table 2) was separated and analyzed from a metamorphic rock of Zone III. It is excluded from the general series of analyses Nos. 1–8, for the host-rock of the pyralspite is somewhat extraordinary in bulk composition.

Host-rock of pyralspite A: Pyralspite-porphyroblast-bearing leucocratic gneiss from Iriyama, Takanuki-mura (Specimen No. AM510813—4). It is a medium-grained leucocratic gneiss mainly composed of quartz, oligoclase, and microcline, with very small quantities

Table 2. Pyralspites from pelitic metamorphic rocks of the Gosaisyo-Takanuki district

Zone for Ca-*rich rocks*		I		II	III			IV		III
Anal. No.		1	2	3	4	5	6	7	8	A
Pyralspite	wt.% MnO	19·74	16·22	11·86	8·09	6·0	5·81	5·70	2·87	5·93
	wt.% FeO	13·39	14·01	16·48	19·39		26·64	26·05	29·62	26·50
	wt.% Sp	46·0	37·8	27·6	18·8	14·0	13·5	13·3	6·7	13·8
	wt.% Alm	30·9	32·3	38·0	44·8		61·5	60·2	68·4	61·2
	Edge length (in kX)	11·63	11·60	11·60			11·53		11·50	11·51
	Refr. index n_D	1·798	1·801	1·799	1·809	1·810	1·810	1·810	1·809	1·815
Associated biotite	wt.% MnO		0·42		0·32		0·23		0·05	
	Refr. index γ_D	1·647	1·660	1·639	1·643	1·652	1·647	1·648	1·641	

Note: In Table 3 are shown complete analyses of pyralspites Nos. 2 and 8, together with those of the associated biotites.

of muscovite, biotite, and pyralspite. Pyralspite occurs in large idiomorphic porphyroblasts, sometimes reaching 4 mm in diameter. Pyralspite occupies about 1% of the rock, and biotite about 0·5%. Thus, the quantity of pyralspite in this rock is larger than that of biotite. As the pyralspite contains 5·93% MnO, the Mn^{+2}: $(Fe^{+2} + Mg^{+2})$ ratio of the host-rock must be somewhat higher than that of ordinary pelitic metamorphic rocks.

Table 3. Pyralspites and associated biotites from the Gosaisyo-Takanuki district

Anal. No.	*No. 2*		*No. 8*	
	Pyralspite	*Biotite*	*Pyralspite*	*Biotite*
SiO_2	36·86	35·88	37·66	36·01
Al_2O_3	21·95	18·52	20·30	18·65
TiO_2	0·61	0·35	0·42	2·74
Fe_2O_3	2·47	8·85	1·75	3·46
FeO	14·01	13·67	29·62	16·36
MgO	1·21	9·06	3·88	8·31
MnO	16·22	0·42	2·87	0·05
CaO	5·95	0·09	2·50	0·11
Na_2O	n.d.	0·82	n.d.	0·97
K_2O	n.d.	6·24	n.d.	8·57
H_2O+	n.d.	5·72	n.d.	2·21
H_2O-	0·18	0·72	0·26	1·89
Total	99·46	100·35	99·26	99·33
Edge length (in kX)	11·60		11·50	
Pyralspite n_D	1·801		1·809	
Biotite γ_D		1·660		1·641

No.2: From pyralspite-bearing biotite schist from Nyuzyo, Iritono-mura (Specimen No. AM501020—10b).

No. 8: From pyralspite-bearing biotite gneiss from Hottyuka, Samegawa-mura (Specimen No. AM491115—35).

(4) *Pyralspites*

(A) *Methods of investigation*—The pyralspites were separated from their host-rocks by means of the electromagnetic separator and Clerici solution. Chemical analyses were carried out by Tami Miyashiro. The MnO contents of the analyzed pyralspites Nos. 2 and 8 in Table 2 were determined by the gravimetric method, being checked by the colorimetric method, while those of the others were determined by the colorimetric method alone. Most of the FeO contents were determined repeatedly. The edge lengths of the unit cell of these pyralspites were measured by the method of X-ray powder photography using a Cu anti-cathode ($K\alpha = 1·539$ kX) and a camera with radius of 5·68 cm. Their refractive indices were measured by the immersion method.

(B) *Results*—In Tables 2–5 are given the results obtained. The Analyses, Nos. 1–8, are numbered in the order of increasing metamorphic grade of their host-rocks.

Table 4. Atomic proportions of pyralspites Nos. 2 and 8, with those of associated biotites, recalculated from Table 3

Basis	*Pyralspite No. 2*	*Pyralspite No. 8*	*Biotite No. 2*	*Biotite No. 8*
	O = 12	O = 12	(O, OH, F) = 24	(O, OH, F) = 24
Si	2·96 } 3·00	3·02	5·24 } 8·00	5·65 } 8·00
Al	0·04 }	0·00	2·76 }	2·35 }
Al	2·03 } 2·00	1·92 } 2·00	0·43 }	1·09 }
Ti	0·04 }	0·03 }	0·04 }	0·32 }
Fe^{+3}	0·15 }	0·11 }	0·97 } 5·14	0·41 } 5·91
Fe^{+2}	0·94 } 2·91	1·99 }	1·67 }	2·14 }
Mg	0·14 }	0·46 } 2·92	1·98 }	1·94 }
Mn	1·10 }	0·20 }	0·05 }	0·01 }
Ca	0·51 }	0·21 }	0·01 }	0·02 }
Na			0·23 } 1·40	0·30 } 2·03
K			1·16 }	1·71 }
OH			5·51	2·31
Mol. % Sp	40·8	6·8		
Mol. % Alm	34·8	69·5		
Mol. % Py	5·4	16·2		
Mol. % Gr	10·7	2·0		
Mol. % And	8·3	5·5		
Edge length (calc.)	11·62	11·54		
Edge length (mes.)	11·60	11·50		
n_D (calc.)	1·807	1·807		
n_D (mes.)	1·801	1·809		

Note: The edge lengths of unit cell and the refractive indices of the pyralspites were calculated on the assumption that they vary linearly with the molecular percentages of constituent molecules whose constants are given by Fleischer [9].

Table 2 shows that *the* MnO *content of pyralspites in ordinary pelitic metamorphic rocks of the Gosaisyo-Takanuki district decreases regularly with the increase in metamorphic grade of their host-rocks.* The decrease in MnO content is so regular as to enable us roughly to draw iso-MnO lines for pyralspite on the geological map of the district as shown in Fig. 1. The boundary between Zones I and II coincides roughly with the 15% MnO line for pyralspite in ordinary pelitic metamorphic rocks, that between Zones II and III roughly with the 10% MnO line, and that between Zones III and IV roughly with the 5·7% MnO line. The decrease in MnO content is accompanied by the increase in FeO content. Thus pyralspite varies from members rich in Sp to those rich in Alm.

The edge length of the unit cell of the pyralspites generally shortens with advancing metamorphism. In Table 5 are given the progressive variations of the spacings of various lattice planes of the mineral. The refractive index of the pyralspite increases generally with advancing metamorphism.

The analyzed pyralspite A has come from the area of Zone III for calcium-rich rocks and has a composition roughly similar to the other analyzed pyralspites

Table 5. Interplanar spacings of pyralspites from the Gosaisyo-Takanuki district (in kX)

Indices	*Intensities*	*Analysis number*					
		1	2	3	6	8	*A*
400	S	2·91	2·90	2·90	2·88	2·87	2·88
420	VS	2·60	2·59	2·59	2·58	2·57	2·57
422	M or W	2·372	2·366	2·367	2·352	2·350	2·350
431	W	2·280	2·275	2·275	2·261	2·260	2·260
521	W	2·125	2·118	2·119	2·107	2·100	2·100
532, 611	M	1·885	1·880	1·880	1·871	1·865	1·865
444	M or W	1·678	1·675	1·675	1·665	1·660	1·660
640	S or M	1·613	1·609	1·609	1·598	1·596	1·596
642	S or M	1·554	1·550	1·550	1·539	1·535	1·537
800	VW	1·455	1·450	1·450	1·440	1·438	1·438
840	VW	1·301	1·298	1·298	1·289	1·287	1·287
842	W	1·270	1·267	1·267	1·257	1·255	1·256
Edge length		11·63	11·60	11·60	11·53	11·50	11·51

of the Zone (Nos. 4–6), though the host-rock of the pyralspite A is somewhat different in composition from ordinary pelitic metamorphic rocks.

(5) *Associated biotites*

Mn^{+2}, Fe^{+2}, and Mg^{+2} are distributed between pyralspite and associated biotite, besides small quantities of associated other ferromagnesian minerals if present.

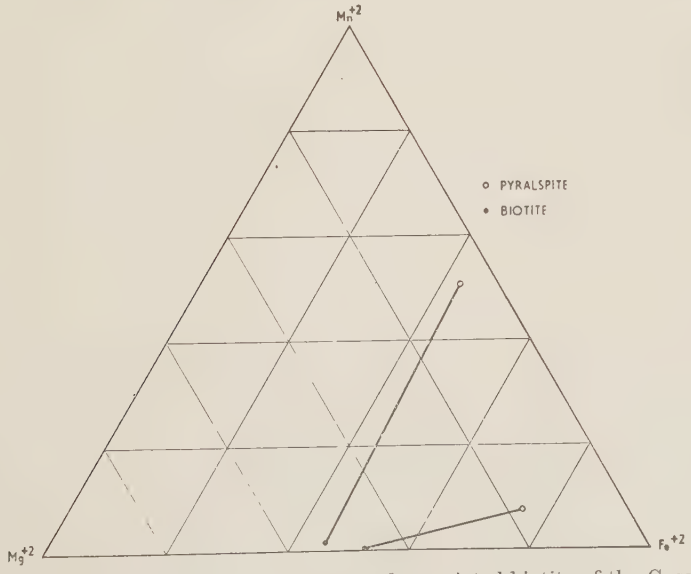

Fig. 3. Composition relations between pyralspite and associated biotite of the Gosaisyo-Takanuki district (atomic proportion)

Four of the associated biotites were also analyzed by Tami Miyashiro completely or partially, and are shown in Tables 2–4 and in Fig. 3. Mn^{+2} present in the rocks is highly concentrated in pyralspite, while Mg^{+2} is concentrated in associated biotite. Fe^{+2} is distributed differently in different cases between the two minerals.

It is a remarkable fact that *the* MnO *content of the biotites which are associated with pyralspites in pelitic metamorphic rocks also decreases regularly with advancing metamorphism of the host-rocks*, as shown in Table 2. Accordingly, as is evident

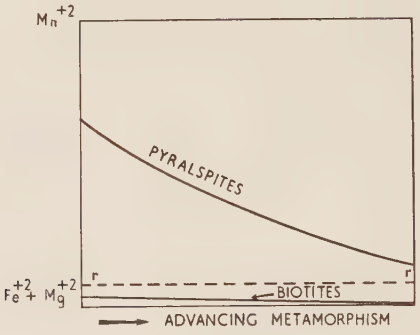

Fig. 4. The variation in composition of pyralspite and associated biotite with advancing metamorphism (Schematic diagram)

from a schematic diagram (Fig. 4), the proportion of pyralspite to associated biotite must increase with advancing metamorphism when the chemical composition (especially the MnO content) of the host-rock remains constant. The dotted line r—r in Fig. 4. represents an example of an isochemical series of pelitic metamorphic rocks. The quantity of pyralspite present in a particular rock is closely related to the MnO content of the rock. This is in accord with observed facts. The MnO contents of the host-rocks of the analyzed pyralspites of the Gosaisyo-Takanuki district are shown in Table 6, together with the quantities of pyralspite and biotite in them. The MnO contents of the host-rocks of the analyzed pyralspites Nos. 1 and 2 were determined directly, while those of the host-rocks of the analyzed pyralspites Nos. 4, 6, and 8 were calculated from the compositions

Table 6. *MnO contents of the host-rocks of the analyzed pyralspites of the Gosaisyo-Takanuki district*

Anal. No.	1	2	4	6	8
Pyralspite (vol. %) . .	1·0	1·6	1	5	1
Biotite (vol. %) . . .	23	15	10	18	12
MnO of the rock (wt. %)	0·41 (D)	0·45 (D)	0·16 (C)	0·46 (C)	0·05 (C)

Note: D = directly determined; C = calculated on the rough assumption that the density of pyralspites is 4·1, that of biotites is 3·1, and that of their host-rocks is 2·8.

and quantities of pyralspite and biotite in them, for the Mn present may be regarded as being contained almost exclusively in these two minerals. (The host-rock of the analyzed pyralspite No. 5 was not shown in Table 6, for the bulk of the biotite present in the rock is probably not in equilibrium with the pyralspite of the rock as was stated before.) The host-rocks of the analyzed pyralspites Nos. 1, 2, and 6 contain roughly similar quantities of MnO, while their pyralspite content becomes progressively remarkably larger with advancing metamorphism. The host-rocks of the analyzed pyralspites Nos. 4 and 8 contain similar quantities of pyralspite, while the higher-grade rock contains a smaller quantity of MnO than the lower-grade one.

3. Pyralspite in Ordinary Pelitic Metamorphic Rocks and a Classification of Metamorphism

(1) *Introductory statement*

So far as the writer is aware, more or less systematic data on pyralspite in a metamorphic district have been reported only from two localities, that is, from the Stavanger district in Norway by Goldschmidt [7] in 1920 and from Dutchess County in U.S.A. by Barth [8] in 1936. In this chapter the writer compares the data of the Gosaisyo-Takanuki district with those of the Stavanger district and Dutchess County, in order to show that the MnO content of pyralspite in ordinary pelitic metamorphic rocks generally decreases with the increase in metamorphic grade, and that, when we use main mineral facies as a scale of metamorphic grade, the MnO contents of pyralspite in ordinary pelitic metamorphic rocks of the same mineral facies differ in different districts, owing to the difference in character of metamorphism in different districts. Thus it will become evident that the MnO contents of pyralspites in ordinary pelitic metamorphic rocks are a useful indicator of the character of metamorphism.

(2) *Comparison of the Gosaisyo-Takanuki district with the Stavanger district*

In the Stavanger district pyralspite occurs widely in pelitic metamorphic rocks. Low-grade pyralspite of the district is manganiferous as is shown in Table 7. With advancing grade in metamorphism pyralspite becomes poorer in MnO and richer in FeO, as in the case of the Gosaisyo-Takanuki district. The chemical compositions of the host-rocks* are similar to those of the Gosaisyo-Takanuki district, as is shown in Fig. 2. The edge lengths of the unit cell and the refractive indices of the analyzed pyralspites were not measured by Goldschmidt. The writer calculated them by assuming that they vary linearly with the molecular percentages of constituent molecules, whose constants are given by Fleischer [9]. The result of the calculation is shown also in Table 7. Thus the shortening of edge length and the increase of refractive index of the mineral with advancing metamorphism are noticed to a small degree in this case also.

If we compare the above variation in composition of pyralspite with that in the Gosaisyo-Takanuki district, we can easily find a difference between the two.

* Injection gneisses of the Stavanger district are not treated here, for they have remarkably higher Fe^{+2}/Mg^{+2} ratios than lower-grade rocks from which all the analyzed pyralspites were separated.

Table 7. Pyralspites from pelitic metamorphic rocks of the Stavanger district

		Lower grade ——→ *Higher*			
		I	II	III	IV
Wt. %	MnO	12·28	6·60	4·57	1·02
	FeO	24·34	28·71	29·74	30·83
Mol. %	Sp	28·5	16·4	10·9	2·6
	Alm.	55·7	70·3	70·2	78·0
	Py	3·4	4·6	11·7	6·8
	Gr	8·3	0·6	0·0	8·2
	And.	4·1	8·1	7·2	4·4
Edge length in kX (calc.)		11·57	11·56	11·54	11·55
Refr. index n_D (calc.)		1·813	1·824	1·815	1·817

I. From quartz-muscovite-chlorite-garnet phyllite.
II. From a rock on the biotite-isograd.
III. From quartz-muscovite-biotite phyllite.
IV. From coarse-grained garnet-mica schist.

In the Gosaisyo-Takanuki district the two lowest-grade pyralspites analyzed were from rocks of the epidote-amphibolite facies, and contain as much as about 20% and 16% MnO. Even the pyralspite from a rock of the lower-grade part of the amphibolite facies, contains more than 8% MnO (No. 4 in Table 2). On the other hand, in the Stavanger district, the two lowest-grade pyralspites analyzed were probably from rocks of the greenschist facies, and contain only 12% and 6% MnO. Pyralspites in pelitic metamorphic rocks of the epidote-amphibolite facies in the Stavanger district have an MnO content of less than 6%. Thus Stavanger pyralspites are generally much poorer in MnO than Gosaisyo-Takanuki pyralspites in ordinary pelitic metamorphic rocks of the same mineral facies. Though the mineral facies relations are not sufficiently known in the Stavanger district*, the writer shows roughly the essential feature of the difference in Fig. 5, by adopting the Eskola's [6] mineral facies as a scale of metamorphic grade.

(3) *Comparison of the Gosaisyo-Takanuki district with Dutchess County*

In Dutchess County pyralspite is nearly constant in composition from its first entrance to the highest grade. It is rich in FeO and is very poor in MnO. The MnO content is 0·3 — 1·8% by weight (0·7 — 4·2% Sp by weight). The refractive index is always 1·810 ± 0·005. The edge length of the unit cell of a pyralspite was found to be 11·59 kX. The chemical compositions of pyralspite-bearing pelitic metamorphic rocks of Dutchess County are shown in Fig. 2.

Thus Dutchess County pyralspites are generally much poorer in MnO than Gosaisyo-Takanuki pyralspites and Stavanger pyralspites in ordinary pelitic

* In the Stavanger district epidote-clinozoisite occurs abundantly and plagioclase contains less than 30% An, up to the highest grade. Common hornblende and clinopyroxene also occur. Therefore, rocks of the highest grade in the district probably belong to the lower-grade part of the amphibolite facies or to the higher-grade part of the epidote-amphibolite facies, depending upon the definition of these mineral facies.

metamorphic rocks of the same mineral facies*, as is shown in Fig. 5. The fact that Dutchess County pyralspites are very poor in MnO from their first entrance to the highest grade, is in harmony with the gradual decrease in MnO content of pyralspite in the Gosaisyo-Takanuki and the Stavanger districts, if we interpret the fact as follows. In Dutchess County the decrease in MnO content of pyralspite with advancing metamorphism may be regarded as having been almost finished before the actually observed garnet isograd. In other words, if there were some

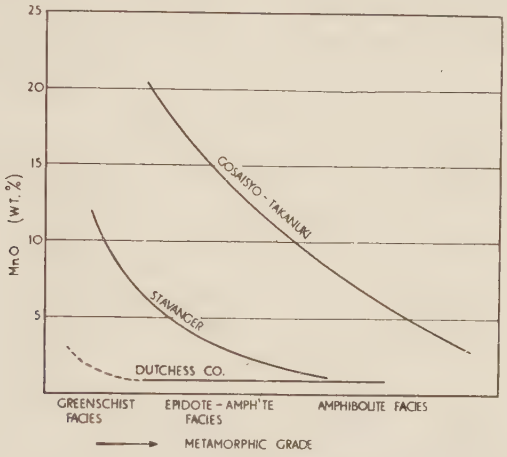

Fig. 5. Pyralspite variation diagram

rocks which had compositions more appropriate for the formation of pyralspite than the rocks actually present, the garnet isograd would be at a lower grade than it is, and so the decrease in MnO content of pyralspite might be observed at the low-grade part of the district, as is shown hypothetically in Fig. 5 by a dotted line.

(4) *Mineralogical characters of metamorphism*

Thus, the MnO content of pyralspites in ordinary pelitic metamorphic rocks generally decreases with the increase in metamorphic grade, but the MnO contents of pyralspites in ordinary pelitic metamorphic rocks of the same mineral facies differ in different districts. The difference is well shown by that in the height of MnO curves for those districts in Fig. 5. The difference may be interpreted to be a result of the difference in character of metamorphism in those districts.

The difference in character of metamorphism of those districts reveals itself also in other mineralogical characters of the metamorphic rocks developed there, as shown in Table 8. The first three columns of the table are arranged in the order of increasing height of the MnO curve for each district in Fig. 5. The table represents mineralogical characters, not of any particular rock or any particular zone, but of the whole metamorphic rock series of the districts from lower grade to the highest. For comparison, the writer shows characteristic minerals of ordinary thermal metamorphism in the fourth column of Table 8.

* Barth's [8] nomenclature of mineral facies differs from Eskola's [6], which the writer adopts in this paper.

It is evident from the table that the kinds of minerals in metamorphic rocks of Dutchess County differ very much from those of ordinary thermal-metamorphic

Table 8. Comparison of almandinous metamorphism with intermediate and non-almandinous metamorphism

District . . .	Dutchess County	Stavanger	Gosaisyo-Takanuki	Ordinary thermal metamorphism
Pyralspite . . .	Abundant; poor in Mn	Abundant; fairly poor in Mn	Sporadic; fairly rich in Mn	Usually absent; if present, rich in Mn
Mineralogical character . .	Almandinous	Fairly almand.	Intermediate	Non-almandinous
Kyanite . . .	+	−	−	−
Staurolite . . .	+	−	−	−
Chloritoid . . .	+	+	−	−
Sillimanite . .	+	+	+	Usually −
Cordierite . . .	−	−	+	+
Andalusite . .	−	−	− (?)	+

Note: + present; − absent.

rocks, while those in metamorphic rocks of the Gosaisyo-Takanuki district resemble to some extent those of ordinary thermal-metamorphic rocks. The Stavanger district is intermediate not only in the height of the MnO curve in Fig. 5 but also in other mineralogical characters, between Dutchess County and the Gosaisyo-Takanuki district. The four columns of Table 8 make a series of regular variation in mineralogical characters.

The mode of occurrence of pyralspite in ordinary thermal-metamorphic rocks will be briefly surveyed below. As is well known, in thermal-metamorphic rocks pyrope never occurs, and almandine does not occur ordinarily*. Almandine was not found in classical hornfels areas such as Kristiania and Comrie. When certain almandine-bearing mica schists were thermally metamorphosed, the almandine was observed to be replaced by pseudomorphs of cordierite and magnetite. These facts suggest that pyrope and almandine are not stable in ordinary thermal metamorphism. On the other hand, Mn-rich pyralspites occur not infrequently in hornfelses (Nos. 1–4 in Table 9). Tilley [10] has laid stress upon the presence of MnO as promoting the formation of pyralspite in contact-zones of pelites. Thus the MnO curves in Fig. 5 for ordinary thermal metamorphism would lie in still higher positions than that for the metamorphism of the Gosaisyo-Takanuki district, if they were plotted.

These facts show that the height of an MnO curve in Fig. 5 serves as an indicator of the mineralogical character of the metamorphism which produced the pyralspites concerned. *The higher the position of the MnO curve, the nearer to ordinary thermal metamorphism is the metamorphism corresponding to it.* Thus the metamorphism

* Exceptional cases where almandine occurs in hornfels will be treated in the next section.

may be classified mineralogically according to the height of the MnO curve for it in Fig. 5. Such diagrams as Fig. 5 will be referred to as "*pyralspite variation diagram*" on later pages of this paper. In the pyralspite variation diagram, the ordinate represents MnO contents of pyralspites in ordinary pelitic metamorphic rocks, while the abscissa represents metamorphic grade.

Table 9. *Pyralspites from hornfelses*

Nos.	*Atomic %*			*wt. %*	*Host-rocks*	*Authors*
	Mn^{+2}	Fe^{+2}	Mg^{+2}	CaO		
1	83·8	13·9	2·3	3·98	Manganiferous hornfels	Yoshimura [27]
2	82·2	12·9	4·9	4·77	Manganiferous hornfels	Yoshimura [27]
3	75·0	23·2	1·8	7·35	Manganiferous hornfels	Yoshimura [27]
4	50·6	39·3	10·1	3·49	Garnet-hornfels	Sollas [28]
5	37·6	54·6	7·8	1·60	Garnet-sill.-hornfels	Tilley [10]
6	7·8	88·5	3·7	1·80	Hornfels	Gottfried [29]
7	4·7	73·8	21·5	1·57	Andal.-sill.-cordier.-gar.-hornfels	Klemm [30]
8	4·3	79·1	16·6	1·61	Gar.-spin.-cordier.-plag.-biotite-hornfels	Stewart [31]
9	2·3	79·7	18·0	(1·72)	Garnet-cordier.-hornfels	Preclik [32]
10	1·7	95·3	3·0	1·68	Garnet-grunerite-cordier.-hornfels	Alderman [33]

Note: $Mn^{+2} + Fe^{+2} + Mg^{+2} = 100$.

Thus there is no natural demarcation line in various kinds of metamorphism of various districts. There is a continuous gradation between such metamorphism as that of Dutchess County on the one hand and ordinary thermal metamorphism on the other.

In order to represent the above mineralogical characters of metamorphism, the writer will use for convenience the new terms "*almandinous*" and "*non-almandinous.*" Almandinous metamorphism is that whose MnO curve lies low in a pyralspite variation diagram such as Fig. 5, while non-almandinous metamorphism is that whose MnO curve is high. Thus in almandinous metamorphism pyralspite rich in the almandine molecule is formed even at relatively low grades in ordinary pelitic metamorphic rocks, while in non-almandinous metamorphism pyralspite rich in the almandine molecule cannot be formed even at higher grades. The metamorphism of the Gosaisyo-Takanuki district is more almandinous than ordinary thermal metamorphism, while it is more non-almandinous than the metamorphism of the Stavanger district and of Dutchess County.

The term almandinous must be carefully distinguished from almandine-rich or garnetiferous. The terms almandinous and non-almandinous denote those mineralogical characters of a series of metamorphic rocks of a district which can be attributed neither to the chemical compositions of rocks developed there, nor to the difference in metamorphic grade within a series of metamorphic rocks. On the other hand the term almandine-rich or garnetiferous denotes the abundance of almandine or presence of any garnet in a rock and is related not only to the

physical conditions under which the rock was produced, but also to the chemical composition of the rock. A rock may well be called an almandinous-metamorphic rock when it was formed by almandinous metamorphism, even if it does not contain any garnet.

Almandinous metamorphism produces kyanite, staurolite, etc., in rocks of appropriate compositions and grades, while non-almandinous one andalusite, cordierite, etc., in rocks of appropriate compositions and grades.

(5) *Classification of metamorphism*

Metamorphism may be classified as almandinous or non-almandinous mineralogically, as kinetic or static according to the presence or absence of deformational movement during metamorphism, and as regional or local according to its areal extent. Various combinations of these categories are possible. For example, some examples of almandinous metamorphism may be kinetic and others static.

The following two combinations are perhaps those most frequently met with in nature:—

(1) Almandinous, kinetic, and regional.
(2) Non-almandinous, static, and local.

Harker's [11] "normal regional" and "purely thermal" metamorphism corresponds roughly to the above two combinations respectively. Two other combinations will be briefly commented on below.

(A) *Intermediate or fairly almandinous, static metamorphism*—As was stated in the preceding section, hornfelses of ordinary thermal metamorphism contain neither pyrope nor almandine. However, rather rarely, there exist extraordinary hornfels areas that have almandine. Such were described, for example, from Gadernheim (No. 7 in Table 9), Carn Chuinneag (Pyralspite: MnO = 0·72%, FeO = 32·40%), Belhelvie (No. 8 in Table 9), and Land's End (No. 10 in Table 9). Some of the almandine-bearing hornfelses may have been produced by fairly non-almandinous metamorphism, when the temperature of the rocks during metamorphism becomes so high as to make the composition of pyralspite in them approach the composition of pure almandine, or when the chemical compositions of the rocks are extraordinary. But other almandine-bearing hornfelses have probably been produced by intermediate or fairly almandinous, static metamorphism, judging from the fact that the Carn Chuinneag almandine is associated with kyanite.

(B) *Intermediate or fairly non-almandinous, kinetic metamorphism of regional extension*—To this group may belong the metamorphism of the Gosaisyo-Takanuki district. The metamorphism of the Tukuba district, studied by Sugi [12], may well also be cited here. He found there three metamorphic zones from lower grades to granitic contact as follows: the zone of spotted biotite slate, that of schistose "hornfels," and that of injection gneiss. The zone of schistose "hornfels" contains andalusite and cordierite, while the injection gneiss has sillimanite and cordierite. The two higher-grade zones belong to the amphibolite facies, judging from the fact that they both have calcium-rich hornfelses composed of labradorite or bytownite, diopside, green hornblende, etc., as intercalated layers between

metamorphic rocks of pelitic type. Pyralspite was not found in any zone, not to speak of kyanite or staurolite.

Similar metamorphic rocks are exposed in various districts in the Inner Zone of Southwest Japan, and have been generally called the Ryoke Metamorphics. In the Ryoke Metamorphics of certain districts, rather small quantities of pyralspite were found in pelitic metamorphic rocks. For example, in the Dando district, the main metamorphic rocks may be divided from lower to higher grade into the following three zones: the zone of "schistose hornfels," which contains andalusite and cordierite (without pyralspite), that of transitional rocks, and that of "banded gneiss," which contains sillimanite and pyralspite [13].

(6) *Construction of the pyralspite variation diagrams*

So far as the pyralspite variation diagram is intended to serve to indicate the degree in which a metamorphism is almandinous or non-almandinous, by the height of the MnO curve corresponding to the metamorphism, the scale of its abscissa must be independent of the degree to be indicated. In this connection we may conveniently classify minerals in metamorphic rocks into two groups as follows:—

Group A: Minerals which occur both in almandinous and non-almandinous metamorphism fairly equally, providing recrystallization is sufficiently advanced in the rocks concerned; e.g. quartz, biotite, amphiboles, pyroxenes, apatite, and grandite.

Group B: Minerals which occur only in almandinous or non-almandinous metamorphism, or occur more commonly in one of the two than in the other; e.g. kyanite, staurolite, chloritoid, sillimanite, cordierite, and andalusite.

Of course, there may perhaps be various minerals of intermediate characters between the two. The scale of abscissa of the pyralspite variation diagram must be based only on the mineral facies defined by minerals of Group A. Thus, the exact definition of a group of mineral facies becomes necessary for the construction of the pyralspite variation diagram.

Actually the definitions of some of main mineral facies, such as the epidote-amphibolite facies and the amphibolite facies, given by Eskola [6] [14] appear to be based on minerals of Group A, while those of many of subfacies given by Eskola [6] and Turner [15] appear to be based on subdivisions of the main facies in relation to minerals of Group B. Thus, almandinous series of subfacies may comprise, from lower grade to higher, the muscovite-chlorite subfacies, the biotite-chlorite subfacies, the chloritoid-almandine subfacies, the staurolite-kyanite subfacies, and the sillimanite-almandine subfacies, defined by Turner [15]. Non-almandinous series may comprise, from lower grade to higher, the actinolite-epidote hornfels subfacies and the cordierite-anthophyllite subfacies. The granulite facies and the pyroxene-hornfels facies, defined by Eskola [6], may conceivably be almandinous and non-almandinous subfacies of a high temperature facies respectively. It is hoped that a more systematic nomenclature will be adopted for various mineral facies. The making of more precise and unanimous definitions of boundaries between various mineral facies is necessary for the precise construction of the pyralspite variation diagrams.

Moreover a difficulty occurs when we consider that the water content of a rock during metamorphism cannot be determined from a resultant rock now exposed on the surface of the earth. Higher pressures of water vapour may cause effects similar to those due to lower temperatures with regard to the mineral compositions of metamorphic rocks. Further, members of a solid solution series may differ in stability relations from one another. Accordingly the correlation of mineral facies with particular ranges of physical conditions is a complicated problem, though we may expect at present that the metamorphic grade defined by the main mineral facies based on the minerals of Group A corresponds roughly to the temperature scale in ordinary cases of metamorphism.

4. Progressive Enlargement of the Composition Field in Pyralspite

(1) *Introductory statement*

The gradual decrease in MnO content, accompanied with complementary increase in FeO content, of pyralspite with advancing metamorphism, shown in the preceding chapter, is a regularity observed only when we treat the mineral in ordinary pelitic metamorphic rocks, that is, in rocks of a fairly limited range of compositions alone.

In this chapter the writer intends to show that pyralspite in metamorphic rocks shows a progressive enlargement of its composition field from Mn-rich compositions to Fe-rich ones, and further to Mg-rich ones, with advancing metamorphism, when we treat rocks of much wider range of compositions. For this purpose he will first briefly survey the modes of occurrence of pyralspite in the metamorphic rocks of the world*.

He has compiled a list of the reliable chemical analyses of pyralspites, the characters of whose host-rocks are known. Analyses in which either MnO, FeO, or MgO is not given, were discarded. From them the writer calculated the atomic percentages of Mn^{+2}, Fe^{+2}, and Mg^{+2} so that $Mn^{+2} + Fe^{+2} + Mg^{+2} = 100$. These values represent also molecular percentages of Sp, Alm, and Py respectively, where Sp + Alm + Py = 100. The results of the calculations are shown in Tables 9–13, and Fig. 6. Analyses are arranged in the order of decreasing Mn^{+2} content in Tables 9–12, and in the order of increasing Mg^{+2} content in Table 13. In Fig. 6, the signs represent a classification of the host-rocks.

Table 10. *Pyralspites from rocks of the greenschist facies*

Nos.	*Atomic %*			*wt. %*	*Host-rocks*	*Authors*
	Mn^{+2}	Fe^{+2}	Mg^{+2}	CaO		
1	79·9	16·9	3·2	9·87	Gar.-actin.-magn.-schist	Hutton [34]
2	32·5	63·6	3·9	4·23	Qz.-mus.-chl.-gar.-phyllite	Goldschmidt [7]
3	18·0	77·0	5·0	2·74	Phyllite on the biotite isograd	Goldschmidt [7]

* Most of the papers published during 1942–1949 are not accessible to the writer at present.

(2) *Pyralspites from rocks of the greenschist facies*

In Table 10 and Fig. 6 are shown the chemical compositions of three pyralspites from low-grade schists or phyllites which occur in the chlorite zone or on the biotite isograd of the respective metamorphic areas. These rocks probably belong to the greenschist facies. All these analyses show high contents of Mn^{+2}.

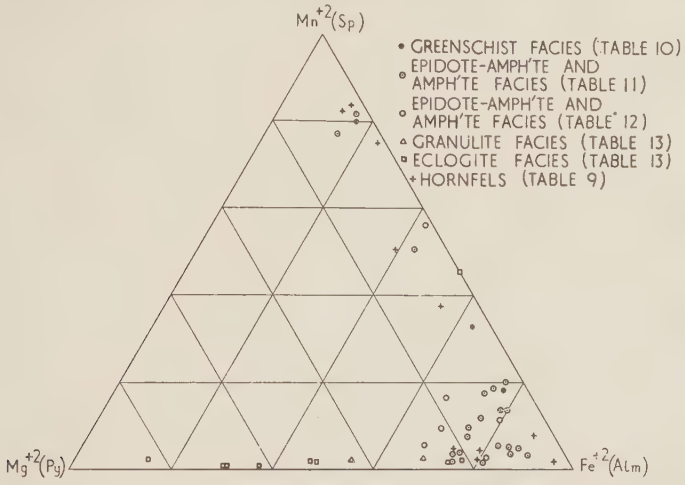

Fig. 6. Pyralspites from metamorphic rocks

The host-rock of the pyralspite from Lake Wakatipu area (No. 1 in Table 10) is highly manganiferous, while those of the pyralspites from the Stavanger district (Nos. 2 and 3) have rather small Mn^{+2} contents (MnO = about 0·4%).

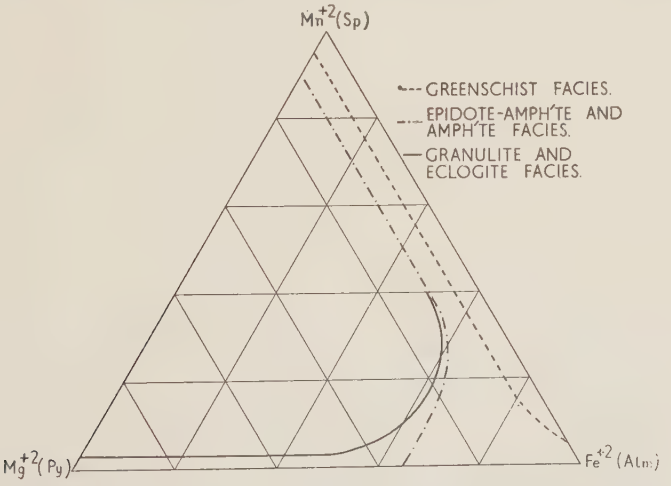

Fig. 7. Progressive enlargement of the composition field in pyralspite

Thus, the composition field of pyralspite in rocks of the greenschist facies may be considered to be an area ranging from the Mn^{+2} apex to near the Fe^{+2} one of the triangle Mn^{+2} — Fe^{+2} — Mg^{+2} as shown in Fig. 7.

Table 11. *Pyralspites from mica schists or allied rocks, probably of the epidote-amphibolite facies or the amphibolite facies*

Nos.	*Atomic %*			*wt. %* CaO	*Host-rocks*	*Authors*
	Mn^{+2}	Fe^{+2}	Mg^{+2}			
1	81·5	16·0	2·5	3·44	Manganiferous part in schistose quartzite	Hietanen [35]
2	77·0	14·3	8·7	5·53	Manganiferous rock assoc. with kyanite schist	Junner [36]
3	50·4	43·0	6·6	5·95	Pyralsp.-biotite-schist	No. 2 in Table 3
4	20·0	76·4	3·6	4·33	Mica-schist	Buttgenbach [37]
5	18·6	74·8	6·6	0·98	Mica-schist	Gossner [38]
6	17·3	73·5	9·2	4·40	Graph.-mica-schist	Simpson [39]
7	13·4	79·2	7·4	1·84	Gar.-biotite-schist	Gorazdowski [40]
8	13·4	80·1	6·5	0·36	Andal.-sill.-gar.-mica-schist	Modell [41]
9	11·8	75·7	12·5	2·41	Mus.-biotite-phyllite	Goldschmidt [7]
10	9·4	74·4	16·2	1·54	Feldsp.-mica-schist	Schumann [42]
11	7·4	75·1	17·5	2·50	Pyralsp.-biotite-gneiss	No. 8 in Table 3
12	5·2	82·5	12·3	3·67	Mica-schist	Du Rietz [43]
13	5·0	84·7	10·3	2·36	Biotite-schist	Wright [44]
14	4·8	86·5	8·7	2·04	Gar.-mus.-schist	Barth [8]
15	3·7	75·5	20·8	1·66	Biotite-schist	Wright [44]
16	3·3	74·3	22·4	0·54	Gar.-biotite-sill.-gneiss	Stewart [45]
17	3·3	85·9	10·8	2·55	Gar.-biotite-sill.-gneiss	Conant [46]
18	3·0	89·3	7·7	3·86	Gar.-mica-schist	Goldschmidt [7]
19	1·5	74·9	23·6	0·16	Gar.-cordier.-sill.-biotite-gneiss	Folinsbee [47]
20	1·2	81·1	17·7	2·08	Graph.-mica-schist	Simpson [39]

Table 12. *Pyralspites from metamorphosed basic rocks of the epidote-amphibolite facies or the amphibolite facies*

Nos.	*Atomic %*			*wt. %* CaO	*Host-rocks*	*Authors*
	Mn^{+2}	Fe^{+2}	Mg^{+2}			
1	56·1	42·4	1·5	1·86	Manganiferous gar.-cummingt.-schist	[48]
2	16·5	66·2	17·3	10·08	Gar.-biotite-clinozois.-alb.-amphibolite	Wiseman [49]
3	11·3	79·9	8·8	4·34	Amphibolite	Simpson [39]
4	9·3	69·1	21·6	6·30	Gar.-hornbl.-schist	Phillips [50]
5	5·5	67·6	26·9	6·44	Gar.-clinozois.-amphibolite	Sato [51]
6	2·3	81·4	16·3	2·48	Gar.-gedr.-cummingt.-amphibolite	Eskola [52]

(3) *Pyralspites from rocks of the epidote-amphibolite facies and of the amphibolite facies*

Most of mica schists and amphibolites, from which analyses of pyralspite were reported, appear to be probably of these two facies, though the detailed study of mineral facies they belong to, has only very rarely been carried out. The pyralspites are shown in Tables 11 and 12, and Fig. 6.

These pyralspites are generally rich in Fe^{+2} and poor in Mn^{+2}. But several of them that came mostly from highly manganiferous rocks are exceptionally rich in Mn^{+2} (Nos. 1, 2, and 3 in Table 11; No. 1 in Table 12). Therefore the composition field of pyralspite appears to be an area ranging from the Mn^{+2} apex to the Fe^{+2} one of the triangle Mn^{+2} — Fe^{+2} — Mg^{+2} as shown in Fig. 7. Thus the composition field in the present two facies is larger than that in the greenschist facies. We may consider that the composition field enlarges gradually with the increase in metamorphic grade.

Actually the composition field of pyralspite may depend not only upon the mineral facies to which the host-rock belongs, but also upon the degree in which the metamorphism that produced the mineral is almandinous. Fig. 7 may be regarded as showing the widest of the composition fields of pyralspite which are realized in various cases of the two facies.

(4) *Pyralspites from rocks of the granulite facies and of the eclogite facies*

(A) *Granulite.* Investigation of pyralspites from rocks of the granulite facies is rare so far as the writer is aware. Only two analyses are shown in Table 13 and Fig. 6. They are rich in Fe^{-2} and Mg^{+2}. One of them (No. G2) is much richer in Mg^{-2} than any pyralspite of the epidote-amphibolite facies and the amphibolite facies.

(B) *Eclogite.* Generally speaking, pyralspites in eclogite are rich in Fe^{+2} and Mg^{-2}, especially in the latter (Table 13 and Fig. 6). As an extraordinary example,

Table 13. *Pyralspites from rocks of the granulite facies or the eclogite facies*

Nos.	*Atomic %*			*wt. %* CaO	*Host-rocks*	*Authors*
	Mn^{+2}	Fe^{+2}	Mg^{+2}			
G1	2·3	68·9	28·8	2·90	Granulite	Rosenbusch-Osann [53]
G2	2·0	54·7	43·3	8·50	Two-pyroxene granulite	Philipsborn [54]
E1	2·1	76·5	21·4	8·61	Eclogite	Eskola [55]
E2	1·7	74·2	24·1	6·21	Eclogite	Eskola [55]
E3	1·7	47·9	50·4	5·22	Eclogite	Eskola [55]
E4	1·8	46·6	51·6	7·2	Eclogite	Alderman [56]
E5	0·9	36·9	62·2	7·98	Kyanite-eclogite	Tilley [17]
E6	0·7	30·6	68·7	9·23	Eclogite	Horikoshi [57]
E7	0·8	30·0	69·2	4·71	Eclogite	Eskola [55]
E8	2·3	14·2	83·5	5·52	Eclogite	Kokta and Nemec [58]

Philipsborn [16] reported a highly manganiferous pyralspite from an eclogite*. A garnet from eclogite described by Mlle Y. Brière [18] is also rather manganiferous (MnO = 4·84%).

(C) *Composition field of pyralspites in the granulite facies and the eclogite facies.* Thus the composition field of pyralspite in the granulite facies and the eclogite facies appears to extend, from compositions rich in Mn^{+2} and Fe^{+2}, towards compositions rich in Mg^{+2}, as shown in Fig. 7. Generally the pyralspite in these facies

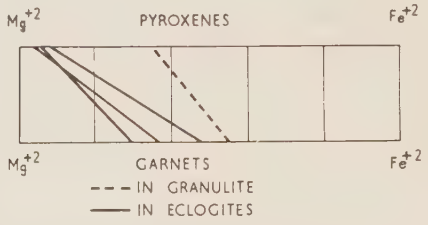

Fig. 8. Composition relations between clinopyroxenes and associated pyralspites

is very poor in Mn^{+2}, for their host-rocks are generally poor in the element. But some of them are exceptionally high in Mn^{+2} as the example of Philipsborn. Accordingly the composition field of pyralspite may be considered to have enlarged in these two facies with advancing metamorphism as compared with that in the epidote-amphibolite facies and the amphibolite facies.

Judging from the present data most of pyralspites from eclogite may be much richer in Mg^{+2} than those from granulite. This fact, however, does not necessarily imply that the composition field of pyralspite in eclogite is much larger towards Mg^{+2}-rich compositions than that in granulite, for it may conceivably have been caused mainly by the fact that eclogite is generally much richer in Mg^{+2} than granulite in bulk composition. Composition relations of pyralspite and associated clinopyroxene in these rocks are shown in Fig. 8 in which are plotted only such clinopyroxenes as contain 3·92% or less Na_2O and such pyralspites as contain 0·72% or less MnO.

(5) *The relation between the progressive enlargement of the composition field and the gradual decrease in MnO content, in pyralspite with advancing metamorphism*

Here will be discussed in detail the relation between the progressive enlargement of the composition field in pyralspite and the before-mentioned gradual decrease of MnO content in pyralspite in ordinary pelitic metamorphic rocks, with advancing metamorphism.

In Fig. 9 is schematically shown an equilibrium relation between pyralspite and associated biotite under a definite physical condition at which the composition field of pyralspite is relatively small. Biotite may possibly contain Mg^{+2} and Fe^{+2} in optional proportions, but does not contain much Mn^{+2}, and so the composition

* Philipsborn's paper was not accessible to the writer. According to Tilley [17], the pyralspite has the following composition: $Sp_{35\cdot3}Alm_{42\cdot5}(Gr + And)_{22\cdot2}$, which is plotted in Fig. 6.

field of biotite is tentatively assumed to be as shown in the diagram. In a rock of composition M, pyralspite M_1 and biotite M_2 may occur in association. In a rock of composition N, pyralspite N_1 and biotite N_2 may occur in association.

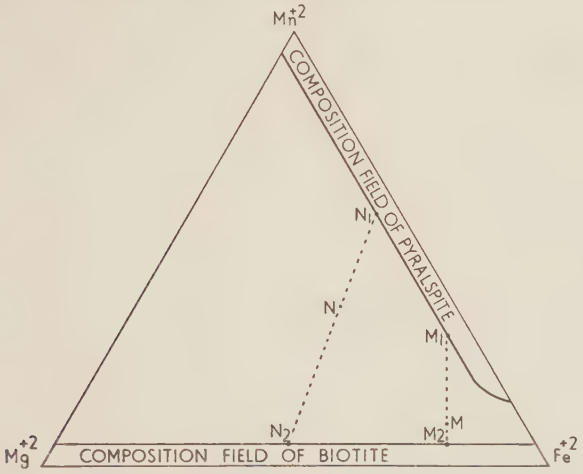

Fig. 9. Equilibrium relations between pyralspites and associated biotites under a definite physical condition (Schematic diagram)

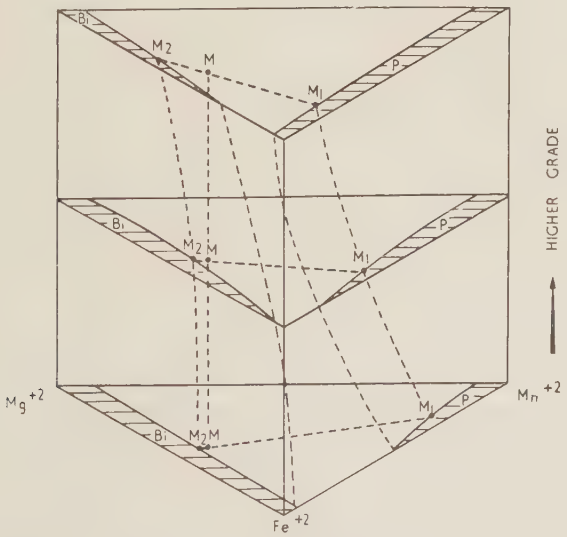

Fig. 10. Equilibrium relations between pyralspites and associated biotites in various metamorphic grades (Schematic diagram)

When the Mn^{+2} content of a pelitic metamorphic rock is so small that the representative point for it in Fig. 9 lies within the composition field of biotite, all the Mn^{+2}, Fe^{+2}, and Mg^{+2} present in the rock may be contained in biotite, without forming pyralspite. When the Mn^{+2} content of a pelitic metamorphic rock is relatively large so that the representative point for it in Fig. 9 lies outside the

composition field of biotite, all the Mn^{+2} present in the rock can not be contained in biotite, and so pyralspite rich in Mn^{+2} may be formed in association with biotite. The MnO content of ordinary pelitic metamorphic rocks ranges from almost zero to about 0·5% by weight, and so some of them may contain pyralspite and others may not under the same physical conditions.

In Fig. 10 is shown schematically equilibrium relations between pyralspite and associated biotite in various metamorphic grades. Pyralspite M_1 is in equilibrium with biotite M_2 in a rock having composition M. P and Bi represent the composition field of pyralspite and of biotite respectively. The composition field of biotite is appropriately assumed in this figure, too. When we treat rocks of a definite composition, for example M in Fig. 10, the enlargement of the composition field in pyralspite with advancing metamorphism may result in the gradual decrease in Mn^{+2} content with a complementary increase in Fe^{+2} content of pyralspite M_1. Accordingly the gradual decrease in MnO content of pyralspite in ordinary pelitic metamorphic rocks with advancing metamorphism may be considered to be a result of the progressive enlargement of the composition field in pyralspite with advancing metamorphism. Thus the difference in the MnO content of pyralspite in pelitic metamorphic rocks of a particular mineral facies in different districts may be, at least partly, due to the difference in the rate of enlargement of the composition field of the mineral in different districts.

So far, the writer has discussed the influence of the proportion of Mn^{+2}, Fe^{+2}, and Mg^{+2} in host-rocks on the composition of pyralspite in them. Other components of the rocks also probably influence the composition of pyralspite in them. Therefore the gradual decrease in MnO content of pyralspite with advancing metamorphism is only an approximate tendency in so far as the host-rocks have a fairly limited range of composition. When we deal with rocks of highly variable compositions, the gradual decrease in MnO content of pyralspite with advancing metamorphism cannot be observed.

5. Crystallo-chemical Explanation

(1) *Introductory statement*

In this chapter the writer intends to show the crystallo-chemical ground for the progressive enlargement of the composition field in pyralspite with advancing metamorphism. The writer's consideration on the crystal chemistry of the mineral will be confirmed by additional proofs concerning the distribution of Mn^{+2}, Fe^{+2}, and Mg^{+2} in pyralspites and associated minerals.

(2) *Crystal chemistry of garnet*

The crystal structure of garnet was worked out by Menzer [19], who confirmed that pyralspite garnet is a solid solution based on ionic replacement among Mn^{+2}, Fe^{+2}, and Mg^{+2}. The Mn^{+2}, Fe^{+2}, and Mg^{+2} ions are situated in interstices within the network composed of linked Si tetrahedra and Al octahedra. Each of the Mn^{+2}, Fe^{+2}, and Mg^{+2} ions is surrounded by eight O^{-2} ions.

Ionic radii in kX are given as follows: Ca^{+2} 1·06; Mn^{+2} 0·91; Fe^{+2} 0·83; Mg^{+2} 0·78. Thus, the immiscibility gap between grandite and pyralspite is probably due to the large difference in ionic radius between Ca^{+2} and Mn^{+2}. The immiscibility

field in pyralspite along the Mn^{+2} — Mg^{+2} side of Fig. 7 is probably due to the large difference in ionic radius between Mn^{+2} and Mg^{+2}.

As was established by Goldschmidt, Bragg, and Pauling, the smaller the metal atom in a crystal is, the smaller is its coordination number, in general. An eight-coordinated position in the crystal structure may be appropriate for such large ions as Ca^{+2} and Mn^{+2} to enter, but is less appropriate for such smaller ions as Fe^{+2} and especially as Mg^{+2}. The ordinary coordination number of Fe^{+2} and Mg^{+2} ions is six.

Thus, it is worthy of note that Mn^{+2}, Fe^{+2}, and Mg^{+2} ions in pyralspite are in eight-coordination*. The pyralspite rich in Mn^{+2} obeys the above general rule about the status of coordination of metal ions, while that rich in Fe^{+2} and especially that rich in Mg^{+2} are exceptional in this respect†. Such an exceptional structure may be expected to have higher potential energy and so generally lower stability.

It is probably due to this fact that pyralspites formed at low temperatures are only those rich in Mn^{+2}, as is shown by the composition field of the mineral in the greenschist facies in Fig. 7. *With the increase in the temperature of its formation, ions, which are less appropriate in ionic radius to enter the crystal structure of pyralspite, become increasingly free to enter the mineral.* Thus the composition field of pyralspite becomes progressively larger, embracing the compositions rich in Fe^{+2}, and later those rich in Mg^{+2}, with advancing metamorphism.

Thus the size of the metal ions, Mn^{+2}, Fe^{+2}, and Mg^{+2} is considered to have a decisive influence upon the stability relations as well as the modes of occurrence of the solid solutions of pyralspite.

(3) *The distribution of Mn^{+2}, Fe^{+2}, and Mg^{+2} in pyralspites and associated minerals*

Pyralspite occurs usually in association with biotite, amphiboles, or pyroxenes in metamorphic rocks as well as in igneous ones. Ions of Mn^{+2}, Fe^{+2}, and Mg^{+2} present in rocks are distributed among associated minerals so that chemical equilibrium among the minerals may be reached on the whole. Crystallo-chemical properties of these minerals may reveal themselves in such distribution of ions.

Distributions of these ions are shown in Tables 14 and 15. Data for the first two pairs in Table 14 were newly prepared through chemical analyses by Tami Miyashiro and are shown more completely in Tables 3 and 4.

The concentration of Mn^{+2} in pyralspite is a strong tendency in all cases. It suggests that the pyralspite structure favours Mn^{+2} in comparison with Fe^{+2} and Mg^{+2} for the crystallo-chemical reason already mentioned.

Of course, not only the crystallo-chemical properties of pyralspite but also those of associated minerals must be taken into account. Detailed examinations of the composition relations between pyralspites and associated ferromagnesian

* Four of the eight O^{-2} ions around an Mn^{+2}, Fe^{+2} or Mg^{+2} ion in pyralspite may be slightly nearer to the central metal ion than the remaining four, and this may perhaps contribute to increase the stability of pyralspite.

† This fact reveals itself also in the extraordinary interatomic distance between Mg^{+2} and O^{-2} in pyrope. Though the determination of parameters of O^{-2} by Menzer is not so precise as to enable us to estimate the distance precisely, the deviation of the measured distance Mg-O from that calculated on the basis of Goldschmidt's standard ionic radius, is too large to be overlooked (the former 2·33 kX; the latter 2·10 kX).

minerals will show how the relations are controlled by the crystallo-chemical properties of the minerals concerned, as follows:—

(A) *Association of pyralspite with biotite* (I, II, and III in Table 14). Mn^{+2}, Fe^{+2}, and Mg^{+2} ions in biotite are in six-coordinated position, which is appropriate for small Mg^{+2} ions to enter, but is not so for larger Mn^{+2} ions, in contrast to the eight-coordinated position in pyralspite. Thus, Mn^{+2} ions are concentrated

Table 14. *Distribution of* Ca^{+2}, Mn^{+2}, Fe^{+2}, *and* Mg^{+2} *in pyralspites and associated ferromagnesian minerals*

(In atomic percentages so that $Ca^{+2} + Mn^{+2} + Fe^{+2} + Mg^{+2} = 100$)

		Ca^{+2}	Mn^{+2}	Fe^{+2}	Mg^{+2}
I	Garnet. . . .	19·0	40·7	34·9	5·4
	Biotite. . . .	0·4	1·4	45·0	53·2
II	Garnet. . . .	7·5	6·8	69·5	16·2
	Biotite. . . .	0·5	0·2	52·1	47·2
III	Garnet. . . .	4·6	4·1	75·5	15·8
	Biotite. . . .	2·2	0·1	56·0	41·7
IV	Garnet. . . .	6·9	2·2	75·7	15·2
	Gedrite . . .	1·4	0·5	55·3	42·8
	Cummingtonite .	2·1	0·4	49·7	47·8
V	Garnet. . . .	6·3	52·5	39·8	1·4
	Cummingtonite .	1·0	10·3	33·4	55·3
VI	Garnet. . . .	23·2	1·6	41·8	33·4
	Hypersthene . .	2·1	0·5	40·7	56·7

I. From pyralspite-bearing biotite schist, Nyuzyo (AM501020—10b). Same as Anal. No. 2 in Table 3.
II. From pyralspite-bearing biotite gneiss, Hottyuka (AM491115—35). Same as Anal No. 8 in Table 3.
III. From garnet-spinel-cordierite-plagioclase-biotite hornfels, Belhelvie. By Stewart [31].
IV. From garnet-gedrite-cummingtonite amphibolite, Isopää. By Eskola [52].
V. From garnet-cummingtonite (manganiferous) schist, Ross and Cromarty [48].
VI. From two-pyroxene granulite, Hartmannsdorf. By Philipsborn [55].

in pyralspite, while Mg^{+2} ions are concentrated in associated biotite. Fe^{+2} ions which are intermediate in ionic radius between Mn^{+2} and Mg^{+2}, are found to be more abundant sometimes in pyralspite, and sometimes in biotite. Ca^{+2} ions are concentrated in pyralspite.

(B) *Association of pyralspite with rhombic amphibole or pyroxene* (IV and VI in Table 14). Rhombic amphibole and pyroxene are similar to biotite in the respect that Mn^{+2}, Fe^{+2}, and Mg^{+2} ions are in six-coordination. Therefore, the distribution of Mn^{+2}, Fe^{+2}, and Mg^{+2} in this case is similar to some extent to that in the above. Ca^{+2} and Mn^{+2} ions which are large, are concentrated in pyralspite, while Mg^{+2} ions which are smaller, are concentrated in associated

Table 15. *Distribution of* Mn^{+2}, Fe^{+2}, *and* Mg^{+2} *in pyralspites and associated ferromagnesian minerals in which* Ca^{+2} *ions are in eight-coordination*

(In atomic percentages so that $Mn^{+2} + Fe^{+2} + Mg^{+2} = 100$)

		Mn^{+2}	Fe^{+2}	Mg^{+2}
I	Garnet	73·9	22·3	3·8
	Actinolite	15·0	36·7	48·3
II	Garnet	16·5	66·2	17·3
	Hornblende	0·7	58·1	41·2
III	Garnet	2·0	54·7	43·3
	Augite	0·8	31·6	67·6
IV	Garnet	91·6	5·5	2·9
	Hedenbergite	17·3	67·6	15·1
V	Garnet	0·8	30·0	69·2
	Clinopyroxene	0·2	6·2	93·6
VI	Garnet	2·1	76·5	21·4
	Clinopyroxene	0·4	30·8	68·8
VII	Garnet	1·7	47·8	50·5
	Clinopyroxene	0·2	9·3	90·5
VIII	Garnet	0·9	36·9	62·2
	Omphacite	0·1	5·1	94·8

I. From garnet-actinolite (manganiferous) vein, Kaso manganese mine. By Yoshimura [27].
II. From garnet-biotite-clinozoisite-albite amphibolite, Loch-na-Craige. By Wiseman [49].
III. From two-pyroxene granulite, Hartmannsdorf. By Philipsborn [55].
IV. From garnet-hedenbergite (manganiferous) mass, Kaso manganese mine. By Yoshimura [27].
V. From eclogite, Almklovdalen. By Eskola [56].
VI. From eclogite, Vanelvsdalen. By Eskola [56].
VII. From eclogite, Silden. By Eskola [56].
VIII. From kyanite eclogite, Weissenstein. By Tilley [17].

rhombic amphibole or pyroxene. Fe^{+2} ions, which are intermediate in ionic radius, are more abundant at least sometimes in pyralspite, though possibly sometimes in rhombic amphibole or pyroxene.

(C) *Association of pyralspite with actinolite or common hornblende* (I and II in Table 15). Ca^{+2} ions, which are in eight-coordination in actinolite and hornblende similarly as in pyralspite, are contained rather abundantly both in actinolite or hornblende and associated pyralspite. Mn^{+2}, Fe^{+2}, and Mg^{+2} ions are in six-coordination in actinolite and hornblende in contrast to being in eight-coordination in pyralspite. Accordingly when actinolite or hornblende is associated with pyralspite Mg^{+2} ions, which are small, are concentrated in actinolite or hornblende, while Mn^{+2} ions which are larger, are concentrated in pyralspite. Fe^{+2} ions are more abundant sometimes in amphiboles, and sometimes in pyralspite.

(D) *Association of pyralspite with cummingtonite* (IV and V in Table 14). Though the crystal structure of grunerite-cummingtonite has not been sufficiently analyzed, a fairly large difference may exist between the structure of grunerite-cummingtonite on the one hand and that of actinolite-hornblende on the other, as suggested below. When cummingtonite is associated with pyralspite, smaller Mg^{+2} ions are concentrated in the former, while not only Mn^{+2} but also Ca^{+2} ions in the latter. This distribution of Ca^{+2} ions differs from that in the above-mentioned case of actinolite-pyralspite or hornblende-pyralspite association, but is similar to that in the case of rhombic amphibole-pyralspite association. It may suggest that cummingtonite differs in crystal structure from actinolite and common hornblende so that Ca^{+2} ions in the former are nearly in six-coordination as in rhombic amphibole.

That the above inference is true, may be confirmed to some extent by the following additional evidence. (*i*) There is a large immiscibility gap between tremolite-actinolite-hornblende on the one hand and grunerite-cummingtonite on the other, as was clearly shown by Sundius [20] [21]. (*ii*) The angle between the cleavage planes (110) is different in tremolite-actinolite-hornblende (55·5°) and in cummingtonite (54·5°) by 1°. It may be a direct manifestation of the difference in crystal structure.

(E) *Association of pyralspite with augite, hedenbergite, or omphacite* (III–VIII in Table 15). In augite, hedenbergite, and omphacite, Ca^{+2} ions are in eight-coordination, while Mn^{+2}, Fe^{+2}, and Mg^{+2} ions are generally in six-coordination, rather as in actinolite and hornblende. Accordingly, the distribution of Ca^{+2}, Mn^{+2}, Fe^{+2}, and Mg^{+2} in this case is similar to that of the actinolite-pyralspite and the hornblende-pyralspite associations. Among Mn^{+2}, Fe^{+2}, and Mg^{+2} ions, Mn^{+2} ions are more abundant in pyralspite, while the smaller Mg^{+2} ions are more abundant in associated augite, hedenbergite or omphacite. Intermediate Fe^{+2} ions are more abundant ordinarily in pyralspite, but rarely in associated pyroxene.

6. Possible Effect of Pressure

In all the preceding statements, the writer has tried to limit, as far as possible, the scope of his discussion to the facts which can be proved directly. However, it may be of some interest to conjecture the physical conditions controlling the mineralogical characters of metamorphism at the end of this paper.

It is frequently stated in literature that garnet is a mineral formed only under high pressures. Indeed, so far as pyralspite rich in Mg^{+2} is concerned, the statement may be justified, for we have no evidence that suggests its being able to be formed under very low pressures. However, concerning pyralspite rich in Mn^{+2}, there is evidence that contradicts the above statement. For example pyralspite rich in Mn^{+2} has been synthesized artificially under atmospheric pressure by Yoder and Keith [22], etc., and has also been found in vesicles in volcanic rocks [23] [24] [25].

Thus Mn^{+2}-rich pyralspite is stable even at very low pressures, while Mg^{+2}-rich pyralspite may not be so. Then we may presumably consider that the composition field of pyralspite may become larger from compositions rich in Mn^{+2}, to those rich in Fe^{+2}, and further to those rich in Mg^{+2}, with increase in pressure,

though we have not sufficient positive evidence for it at present. In other words not only rise in temperature but also rise in pressure may presumably favour the formation of pyralspite in the sense that the composition field of pyralspite in metamorphic rocks becomes larger with their rise. Thus, it is possible if not probable that almandinous metamorphism represents metamorphism under higher pressures than non-almandinous metamorphism.

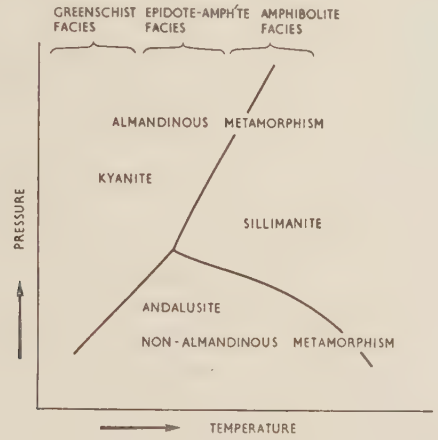

Fig. 11. Probable stability fields of kyanite, sillimanite, and andalusite

In a previous paper [26], the writer has discussed the probable stability relations of andalusite, sillimanite, and kyanite, which are shown in Fig. 11. This diagram is compatible with the above inference. If almandinous metamorphism is the metamorphism under higher pressures, it will produce kyanite in lower grades and sillimanite in higher grades in rocks of appropriate compositions, as shown in the diagram. Intermediate metamorphism may produce sillimanite as in the Gosaisyo-Takanuki district, or otherwise andalusite in the lower grade and sillimanite in the higher as in the Tukuba district [12]. If non-almandinous metamorphism is the metamorphism under lower pressures, it will produce andalusite in rocks of appropriate compositions, except in an extremely high grade where sillimanite may be formed, as in the Comrie district, as shown in the diagram.

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His thanks are due to Prof. M. P. Billings, Prof. R. Kiriyama, Dr. H. S. Yoder, and many other persons, who kindly criticized the writer's views.

References

[1] Ford, W. F.; Amer. J. Sci. 1915 **40** 33–49. [2] Boeke, H. E.; Z. Krist. 1914 **53** 149. [3] Winchell, A. N.; Optical Mineralogy, II, 3rd. ed., New York 1933. [4] Gorai, M.; Mem. Fac. Sci. Kyushu Imp. Univ., Ser. D. 1944 **2** 239–321. [5] Miyashiro, A.; Progressive metamorphism of the calcium-rich rocks of the Gosaisyo-Takanuki district, Abukuma Plateau, Japan. J. Geol. Geogr. 1953 **23** 81-107. [6] Barth, Tom. F. W., Correns, C. W. and Eskola, P.; Die Entstehug der Gesteine, Berlin 1939. [7] Goldschmidt, V. M.; Vidensk. Skr. I mat.-natur.-vet Kl. 1920 **10**. [8] Barth, Tom. F. W.; Geol. Soc. Amer. Bull. 1936 **47** 775–850. [9] Fleischer, M.; Amer. Min. 1937 **22** 751–759. [10] Tilley, C. E.; Min. Mag. 1926 **21** 47–50. [11] Harker, A.; Metamorphism. London 1932. [12] Sugi, K.; Japan. J. Geol. Geogr. 1930 **8** 29–112. [13] Koide, H.; Ass. Geol. Collabor. Monogr. 1949 **3** 1–39. [14] Eskola, P.; Norsk geol. Tidsk. 1920 **6** 143–194. [15] Turner, F. J.; Igneous and Metamorphic Petrology, New York, Toronto and London 1951. [16] Phillipsborn, H. von; Abh. Math.-phys. Kl. Sächs. Akad. Wiss. 1928 **40** 1–43. [17] Tilley, C. E.; Min. Mag. 1936 **24** 422–432 Tab. 1. [18] Brière, Y.; Min. Abstr. 1920 **1** 163. [19] Menzer, G.; Z. Krist. 1929 **69** 300–396. [20] Sundius, N.; Min. Petr. Mit. 1933 **43** 422–440. [21] Sundius, N.; Sveriges geol. undersökning 1944 Ser. C **460** 1–11. [22] Yoder, H. S. and Keith, M. L.; Amer. Min. 1951 **36** 519–533. [23] Cross, W.; Amer. J. Sci. 1886 **31** 432–438. [24] Pabst, A.; Amer. Min. 1938 **23** 101–103. [25] Kozu, S., Kawano, Y. and Yagi, K.; J. Japan. Ass. Petr. Min. Econ. Geol. 1941 **25** 1–12. [26] Miyashiro, A.; J. Geol. Soc. Japan. 1949 **55** 218–223. [27] Yoshimura, T.; J. Geol. Soc. Japan 1938 **45** 133, 134, 170. [28] Sollas, W. J.; Sci. Proc. Dublin Soc. 1891 N. Ser. **7** 49. [29] Gottfried, C.; Fortschr. Mineral. etc. 1933–34 **18** 174. [30] Klemm, G.; Neues Jahrb. f. Mineral. etc. 1922 Ref. **2** 39. [31] Stewart, F. H.; Min. Mag. 1942 **26** 260–266. [32] Preclik, K.; Centralbl. f. Mineral. etc. 1924 652–664. [33] Alderman, A. R.; Min. Mag. 1935 **24** 42–48. [34] Hutton, C. O.; Geol. Mem. Dept. Sci. Indust. Res. New Zealand 1940 **5** 1–84. [35] Hietanen, A.; Bull. Comm. Géol. Finlande 1936 **115** 387–400. [36] Junner, N. R.; Trans. Amer. Inst. Mining Metall. Engin. 1927 **75** 385–395. [37] Buttgenbach, H.; Mém. Acad. R. Belgique Cl. Sci. Ser. 2 1923 **7** 1–36. [38] Gossner, B.; Neues Jahrb. f. Mineral. etc. Beil. Bd. 1931 **64** A 225–233. [39] Simpson, E. S.; J. Roy. Soc. W. Australia 1936–37 **23** 17–35. [40] Gorazdowski, L.; Z. Krist. 1900 **33** 658. [41] Modell, D.; Bull. Geol. Soc. Amer. 1936 **47** 1885–1932. [42] Schumann, H.; Tscherm. Min. Petr. Mitt. 1930 **40** 73–187. [43] Du Rietz, T.; Geol. Fören. Stockholm Förh. 1935 **57** 133–260. [44] Wright, W. I.; Amer. Min. 1938 **23** 436–449. [45] Stewart, F. H.; Min. Mag. 1950 **29** 252–253. [46] Conant, L. C.; Econ. Geol. 1935 **30** 387–399. [47] Folinsbee, R. E.; Amer. Min. 1941 **26** 50–53. [48] Chemical Analyses of Igneous Rocks, Metamorphic Rocks and Minerals, Geol. Survey Great Britain, 1931 Anal. Nos. 586 and 582. [49] Wiseman, J. D. H.; Quart. J. Geol. Soc. London 1934 **90** 354–417. [50] Phillips, F. C.; Min. Mag. 1930 **22** 239–256. [51] Sato, H.; Expl. Text, Geol. Map of Niihama, 1938 17. [52] Eskola, P.; Bull. Comm. Géol. Finlande 1936 **115** 475–487. [53] Rosenbusch, H. and Osann, A.; Elemente der Gesteinslehre 685. Stuttgart 1923. [54] Philipsborn, H. von; Chemie der Erde 1930 **5** 233–253. [55] Eskola, P.; Vidensk. Skr. I mat.-natur. Kl. 1921 **8** 28, 31, 38, 44. [56] Alderman, A. R.; Quart. J. Geol. Soc. London 1936 **92** 488–530. [57] Horikoshi, Y.; J. Geol. Soc. Japan 1937 **44** 141–144. [58] Kokta, J. and Nemec, F.; Min. Abstr. **6** 428.

Geochimica et Cosmochimica Acta, 1953, Vol. 4, pp. 209 to 212. Pergamon Press Ltd., London

Report: Symposium on Geochemistry, Zurich, 11 13 August 1953
Organized by the Commission on Geochemical Localization of the Elements.

The first international symposium on Geochemistry was held in the Mineralogisch-Petrographisches Institut of the Eidgen. Technische Hochschule in Zürich, 11 13 August 1953 under the auspices of the International Union of Chemistry. It was presided over by Dr. M. FLEISCHER and by the local chairman Professor C. BURRI, with Professor T. F. W. BARTH as secretary. Over sixty members representing eighteen countries were present.

Dr. M. FLEISCHER as acting president opened the meeting by paying homage to the memory of Professor P. NIGGLI, the first president of the Commission whose sudden death last winter came as a serious loss to the international field of mineralogy, and a personal bereavement to all of us.

In his presidential report of 1951 Professor NIGGLI, referring to the great importance of geochemistry, especially in nuclear studies, in mining and metallurgy, in agriculture and other fields of pure and applied science, advocated the establishment of a commission and, eventually, a section of geochemistry within the International Union of Chemistry. At the same time he took great care to explain how impossible it is to localize the chemical elements without a thorough knowledge of the geological milieu. The Zürich Symposium is a fruit of NIGGLI's work and we shall carry it out in his spirit. It was peculiarly appropriate to the occasion, as pointed out by

Professor C. BURRI, that the members of the Symposium met in the large lecture room in which Professor NIGGLI gave those lectures that for over thirty-two years inspired generation after generation of students. Those who were privileged to hear these lectures are not likely to forget either the man who gave them or the scientific outlook he presented. How little those who heard him speak with accustomed brilliancy on this spot on the morning of 13 January suspected that that lecture was to be his last, and that the heart-attack he had some hours later was to cause his death on the same afternoon.

1. REPORTS RELATING TO THE PROBLEM OF ORGANIZING, COMPLETING AND MAKING AVAILABLE GEOCHEMICAL DATA

FLEISCHER, MICHAEL: Revision of CLARKE's "Data of Geochemistry" (Bull. 770, U.S. Geol. Survey).

HOOKER, MARJORIE: Revision of Washington's "Chemical Analyses of Igneous Rocks" (Prof. Paper 99, U.S. Geol. Survey).

MÜLLER, WOLFGANG: Die Geochemie im Gmelin-Handbuch. Der Gmelin Informationsdienst als Schrifttumsarchiv für das Gebiet der Geochemie.

RANKAMA, KALERVO: Opening remarks on compilation, revision, organization of geochemical data. Important developments have taken place since C. F. SCHÖNBEIN in 1838 mapped out a research programme of geochemistry. Recent developments have been particularly rapid, and the number of papers of geochemical interest is constantly and rapidly increasing. Unfortunately the published information is widely scattered. Publication of detailed reports and of a geochemical annual review was considered.

ROSBAUD, PAUL: The publication of geochemical papers in *Geochimica et Cosmochimica Acta.*

2. GENERAL LECTURES

GREEN, JACK: Geochemical Table of the Elements for 1953 (read by title), will be printed in *Bull. Geol. Soc. America.*

NODDACK, W.: Energiespeicherung in Mineralien.

TOMKEIEFF, S. I.: Petrochemistry and petrogenesis.

For the study of a large number of chemical analyses of rocks simple statistical methods combined with simple graphic representation should be used. Thus alkali-silica scatter diagrams or variation curves, used in conjunction with silica frequency curves or rock volumes frequency curves, are deemed sufficient for the first generalized characterization of the petrochemical features of a given rock assemblage.

Two British petrographical provinces: (1) Carboniferous-Permian (293 analyses) and (2) Tertiary (333 analyses) were studied by the above method. The nature and amounts of leading rock types of the Tertiary province can be explained by postulating their derivation from the remelt of the earth's crust in which the andesite zone was eliminated during the Caledonian igneous period and part of the basaltic zone during the Carboniferous-Permian igneous period. Hebridean basalt magma type, Causeway basalt magma type, and the Intermediate-Acid magma type are, according to this scheme, derived zones of the earth's crust remaining in place after previous eliminations.

Similar methods applied to the north-western region of the Pacific Ocean (543 analyses) suggest that the volcanic rocks of the Circumpacific arcs belong to the subalkalic suite and range from basalt to liparite, while the rocks of the hinterland belong to the alkalic suite and are predominantly basic. The rocks of the foreland, as represented by the volcanic rocks of Hawaii, belong to both of these suites. Although predominantly subalkalic basalts they also show the development of alkaline rocks, ranging from oligoclase and nepheline basalts to trachytes. A fuller account will be published elsewhere.

TOMKEIEFF, S. I.: The periodic system in geochemistry.

(Will be printed in a forthcoming series of publications the first of which is entitled *A new periodic table of the elements based on the structure of the atom.* Chapman & Hall, London 1953.)

UREY, H. C.: Composition and origin of meteorites.

(Published in *Geochimica et Cosmochimica Acta*, Vol. 4, page 36.)

AHRENS, L. H. (read by BARTH): The lognormal distribution of the elements.

The nature of the distribution of the concentration of an element (at least the rare ones) in specific igneous rock types is definitely not normal (linear scale) but lognormal (geometric scale). Scatter varies numerously from element to element, but the nature of the distribution remains the same (see Fig. 1). Several interesting consequences arise once one has established this basic fact.

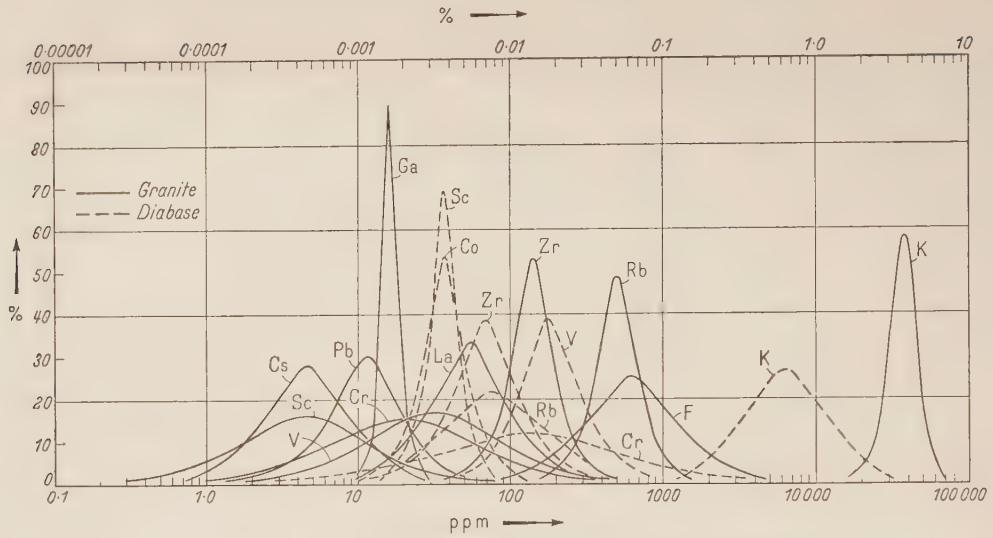


Fig. 1. The frequency distribution of elements in granite and in diabase.

3. Reports on Current Geochemical Research

Barth, T. F. W.: Current geochemical research in the world. Lists of geochemists and their work will be published later.

Contaut, Henri: Sur le comportement de certains sediments en profondeur.
Original lignite contains about 50% volatiles and 5–20% H_2O. Table 1 shows how it reacts on pressure, temperature and time. During the pyrogenation it loses gases and gives a mixture of crude oil and methane. Synthesis of oil by hydrogenation of carbon oxides under pressure will also take place, yielding naphtha and water that may appear at the surface in hot springs. Earthquakes may be caused by high gas pressure at, say, 8–10,000 m depth ; the reduction in volume concomitant of the departure of the volatiles may attain 50–60%. The law of Hilt is verified, consequently, the occurrence of e.g. a type of meagre coal thus indicates that, at the time of its formation, it was buried under 10,000 m sediments.

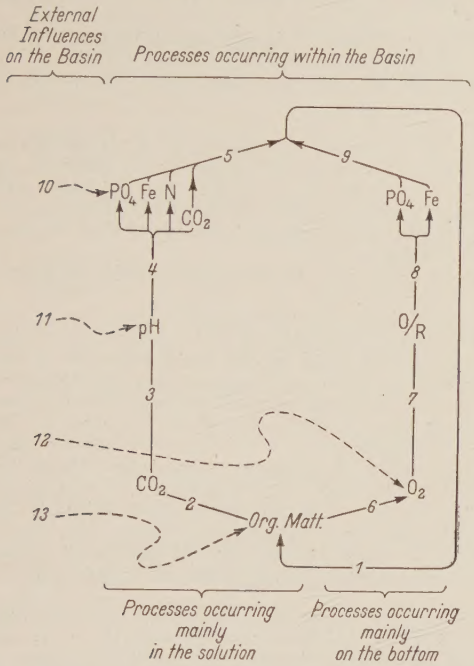
Table 1. *Transformation of lignite slowly sinking into the depths of the crust of the earth*

	Depth in m	*Temp.* C°	*Time in million yrs.*	*Volatiles* %
Lignite	—	—	—	50
Oil	4,000	200	20	45
Oil	6,000	300	30	35–40
Oily coal	8,000	400	40	23–30
Meagre coal	10,000	500	50	12–13
Anthracite	12,000	600	60	4–7
Anthracite	18,000	900	—	0·2–0·3
Reduction of oxides	24,000	1200	—	—

Chalmers, R. A.: Current research in the Department of Geology, University of Durham.
Davidson, C. F.: Associations of uranium with mineral hydrocarbon.
Fairbridge, R. W.: Intertidal Solution of $CaCO_3$.
On limestone cliffs between the limit of high and low tide a notch or undercut is eroded, ultimately leaving a horizontal shore platform or reef at about low tide level. The phenomenon is common in all oceans at warmer latitudes. Four explanations are suggested: Mechanical, chemical, biomechanical, and biochemical. Of these, the biochemical processes seem to be most effective: Inter-tidal fauna and flora produce micro-environments, where *local* acid reaction may occur. Microscopic bluegreen algae bore 1–3 mm below rock surface. An indurated coat of extra-hard calcite, covering the algal erosion "front" indicates precipitation of $CaCO_3$, possibly a process alternating diurnally with solution.
Investigations in progress: In W. Australia: E. P. Hodgkin and L. Marsh (marine moluscan ecology) G. G. Smith (algae); J. Jitts (hydrology); J. Spotts—now at Harvard (mineralogy). In France: Guilcher—Nancy (geomorphology). In America: Ginsburg—at Miami (chemistry); Fosberg—U.S.G.S. (algae); Newell—New York (ecology); Emery—S. California (tide pool chemistry); Revelle (chemistry).
Discussion: Professor Urey believed first job was determination of $CaCO_3$ solubility—was sea-water *really* supersaturated? Professor Correns said he was sure it was supersaturated but agreed that more

precision was required. Professor MILLOT mentioned some contemporary work on CaMg relations by his students at Nancy.

BULJAN, MILJENKO: The system of biochemical circulation of nutrients in water basins.
The diagram of Fig. 2 is a graphic representation of the "Geochemical Circle of Organic Production" and is valid both in the sea and in fresh-water lakes. It shows the relations of organic matter production ($CO_2 + H_2O \rightleftharpoons HCOH + O_2$) to the solubility of nutrient salts, to aeration, oxidation-reduction ($M^{\cdot\cdot\cdot} + e \rightleftharpoons M^{\cdot\cdot}$), and to *pH*-values of the waters ($FePO_4 \overset{H^{\cdot}}{\rightleftharpoons} PO_4^{\prime\prime\prime} + Fe^{\cdot\cdot}$). It is possible to increase the production artificially by (1) addition of nutrient salts, (2) by decrease in *pH*, (3) by decrease of oxygen in the deep water layers.



1. Production = Synthesis of organic compounds.
2. Mineralization of organic compounds.
3. Acidification ⇌ Alkalization.
4. Increase of solubility ⇌ Decrease of solubility.
5. +9 = 1.
6. Consumption of O_2 during the mineralization of organic compounds.
7. Increase ⇌ Decrease of reductive properties of the environment.
8. Reduction ⇌ Oxidation of sediments $FePO_4 + e^- \rightleftharpoons Fe^{\cdot\cdot} + PO_4^{\prime\prime\prime}$
10. Addition of Nutrient Salts
11. Addition of Acid Matter
12. Addition of Reductive Matter
13. Addition of Organic Matter

} from without the basin.

Left hand branch: $Fe^{\cdot\cdot} + PO_4^{\prime\prime\prime} \overset{H^{\cdot}}{\rightleftharpoons} FePO_4$
Right hand branch: $M^{\cdot\cdot\cdot} + e^- = M^{\cdot\cdot}$
Middle: $CO_2 + H_2O = HCOH + O_2$

Fig. 2.

HABERLANDT, HERBERT: Bericht über geochemische Arbeiten in Oesterreich (with A. SCHIENER). Small quantities, down to 10 p.p.m. of Dysprosium, Terbium, Erbium, Samarium, and Europium can be determined qualitatively in the fluorescence spectra of scheelite. Scheelites of different mode of occurrence show marked differences in their content of the rare earths.

HECHT, FRIEDRICH: Uranium contents of the cores of the Swedish Deep-Sea expedition of 1947/48.

HOUTERMANS, F. G.: Isotope abundance of common lead.

INGERSON, EARL (presented by FLEISCHER): Geochemical work of the Geochemistry and Petrology Branch, U.S. Geological Survey.

ISHIBASHI, MASAYOSHI: Regularities of the amounts of elements dissolved in sea water and an attempt of finding the age of the ocean.

LOUIS, MARCEL and F. BIENNER: Les études géochimiques à l'Institut Français de Pétrole.
In order to show the evolution of mineral oils a triangular diagram is used, the corners of which represent asphalt, oily constituents, and resins. The evolution goes from crude oil toward asphalt and is accompanied by a chemical change in the constituent oil whose paraffin character decreases while the molecular weight increases. The results have been used in geochemical prospecting for oil in sedimentary basins.

MIHOLIC, STANKO: Radioactivity of Waters Issuing from Sediments.
In Slovenia and N.W. Croatia a fault stretches for 110 kilometres in a W.–E. direction, cutting Triassic sediments except at two points (at Rimske Toplice and Harina Zlaka) where it cuts Carboniferous strata. A shorter, parallel fault to the South cuts Triassic strata only. Thermal springs are connected with the faults. The average radioactivity of waters from the Triassic is 0·44 mμC/l, while waters from the Carboniferous show much higher values 3·89 mμC/l.

In Eastern Bosnia arsenious spring waters of the Srebrenica old (mediaeval) silver mine on the contact between andesite and Carboniferous schists show high radioactive values: (Great Guber source 7·02 mμC/l and Little Guber source 3·578 mμC/l.)

Eastern Macedonia is dissected by the great Aegean fault and by a number of faults parallel to it. One of them cuts Archaean paragneisses at Mt. Belasica; here a thermal spring (at Banjsko, 71·8°C) gave 1·764 and 1·623 mμC/l. Further to the N.W. the fault dissects Carboniferous schists and gives vent to the thermal waters of Stip (50·3–66·8°C) which show high radioactivity: (4·213–15·59 mμC/l), while acidulated water at Bogoslov (9·4°C) has a radioactivity of 3·346 mμC/l. In contrast to it, at Katlanova, where the fault cuts Oligocene sediments, the thermal waters (39·0°C) are practically non-radioactive (0·0693 mμC/l). It seems that Cretaceous strata, according to a previous investigation, and strata belonging to the Carboniferous and perhaps to the Archaean yield waters of high radioactivity.

Millot, Georges: Les récherches en cours au Laboratoire de Géochimie de Nancy.

Picciotto, E.: Recherches sur la géochimie des éléments radioactifs.

Pitcher, W. S.: Geochemical research at Department of Geology, Imperial College, London.

Schoeller, Henri: L'iode, le brome, le potassium des eaux souterraines et superficielles et des eaux de gisements de pétrole.

The content of iodine seems to be governed by the solubility product of $Ca(IO^3)_2$, which depends upon the nature of the wall rocks and on the concentration of chlorine in the water. The weight ratio I/Cl varies from $0{\cdot}002 \times 10^{-3}$ to 10×10^{-3}, but 55% of the waters are in the range $0{\cdot}05 \times 10^{-3}$ to 1×10^{-3}.

The content of bromine is not limited by the solubility. It depends upon the nature of the wall rocks and on the presence of Cl. The ratio Br/Cl varies from zero to 10×10^{-3}; 50% of the waters are in the range $0{\cdot}1 \times 10^{-3}$ and 2×10^{-3}.

The content of K goes parallel to that of Na, but K/Na decreases with increasing concentration. In practically all waters one finds that sodium (by weight) lies between $Na = 0{\cdot}3\ K^{1,5}$ and $30\ K^{1,5}$.

Neither the concentrations of I, Br, K, nor the ratios I/Cl, Br/Cl, K/Na characterize the waters of petroleum deposits.

Schroll, Erich: Leitelemente in Erzen der Ostalpen.

Ore deposits similar in age and in mode of occurrence show similar associations of trace elements. Sphalerites from the Paleozoic "Altkristallin" contain Hg and Co (in special cases also In and Sn). In ore of the Alpine metallization period the concentrations of In and Sn are small. The Mesozoic ores carry traces of As, Tl, and Ge; but Hg and Co are usually absent. Traces of Bi, In, Sn (indicating elevated temperature) are found in galena and sphalerite of the anticlines, while traces of Ge, Ga, Hg, Tl, indicating low temperatures are found in ores of the synclines.

Schwander, Hans: Sauerstoffisotopenverhältnis in Silikatgesteinen und Mineralien (will be published in this journal).

Urbain, Pierre: Considérations sur le mécanisme de l'altération des feldspaths.

The feldspar minerals are structurally characterized by chains of $Si_xAl_2O_{2\cdot(x+2)}$ and positive ions of low valence whose movements are limited to the interstices between the chains, but whose activities in the free state are rather high. Thus by the alteration of feldspar, mono- and divalent ions are liberated, pass through surface waters, help to sediment a great variety of residual material, and may finally enter into new minerals. These processes are of the utmost importance in the geochemical evolution of the hydrosphere and of the outer lithosphere, and are well worth a closer study: The classical theories have remained in an embryonal stage, and have not considered sufficiently the structural properties of the feldspars; the modern theories have not yet been controlled by experiments (except in the work of C. W. Correns, A. Demelon and E. Batisse, S. K. Dubrovo, A. F. Frederickson, R. L. Folk, E. R. Graham, etc.). It is time now to establish an international programme to coordinate theory and experiment and to further investigate into the mechanism of the alteration of feldspars and feldspathic rocks.

Urbain, Pierre: Les éléments décelables par voie spectrographique dans les eaux thermales et minérales.

Systematic research of the rare elements in the thermal waters of France, particularly to verify the hydrothermal origin of metalliferous veins, was begun in 1912 by J. Bardet on the initiative of L. de Launay and G. Urbain. All in all J. Bardet has found 26 different elements in 65 different thermal waters. Other countries have done the same (e.g. L. de Menezes Correa Acciaiuoli in Portugal, and others). In the following list the index gives the number of places in which the element has been found among a total of 102 places in France and Portugal.

Pb_{78}	Cu_{72}	Sn_{62}	Ge_{61}	Ag_{58}	Ti_{50}	Ba_{42}	Mo_{40}	Be_{40}	Ga_{37}	Zn_{32}	V_{26}	Sb_{25}
Cr_{23}	Bi_{20}	W_{15}	Ni_{15}	Al_{12}	Tl_5	Zr_5	Co_5	Cs_4	Rb_4	Cd_1	Au_1	

in addition, Fe, Mg, Sr are practically always present.

The ionic radius of these elements (except Be, which is smaller, and Rb, Cs, Ag, Au which are larger) lies between 0·5 and 1 Å.

The relative abundance of an element in the thermal waters is different from that in the earth's crust, and depends directly on the nature of the water in which it is found. The nature of the water again depends upon the geological milieu: Waters in areas rejuvenated in Alpine or post-Alpine time seem to be richer in rare elements than waters whose mineralization comes from sedimentary rocks (including salt deposits). Time will show if this rule has general applicability.

Wickman, F. E.: Geochemical work at Stockholm.

Wilson, A. F. (presented by Fairbridge): Current geochemical research in Western Australia.

During the Symposium six members of the Commission on Geochemical Localisation of the Elements of the International Union of Chemistry, who were present at the Symposium, met and, among other business, elected Professor H. C. Urey as a member of the Commission in the place of the late Professor P. Niggli, and Professor C. Burri as an observer attached to the Commission. The composition of the Commission (subject to confirmation by the Committee of the International Union of Chemistry) is as follows: M. Fleischer (Washington), President; T. F. W. Barth (Oslo), Vice-President; K. Rankama (Helsinki), Secretary; and members, H. S. Brown (Pasadena), C. W. Correns (Göttingen), D. Guimaraes (Belo Horizonte), A. Holmes (Edinburgh), E. Raguin (Paris), S. I. Tomkeieff (Newcastle-on-Tyne) and H. C. Urey (Chicago).

After the meeting a group of members of the Symposium took part in an excursion to the Eastern Gotthard Massif (14–15 August) most admirably led by Professor C. Burri, assisted by Dr. H. Mülli.

Invitations for the next meeting, presumably in 1955, were received (1) from Dr. Marcel Roubault, director of the Ecole Nationale Supérieure de Géologie Appliquée et de Prospection Minière at the University of Nancy, and (2) from Professor Harrison Brown, Division of Geological Sciences, California Institute of Technology at Pasadena. Action was deferred pending a statement from the Section of Inorganic Chemistry as to its plans.

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